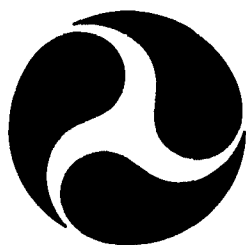


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**U.S. Coast Guard  
1994 Oil Pollution Research Grants  
Publications - Part II**

U.S. Department of Transportation  
Research and Special Programs Administration  
John A. Volpe National Transportation Systems Center  
Cambridge, MA 02142



FINAL REPORT  
September 1996

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Prepared for:

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## **FOREWARD**

### **PUBLICATIONS OF THE U.S. COAST GUARD 1994 OIL POLLUTION RESEARCH GRANTS**

On March 24, 1989 the EXXON VALDEZ ran aground on Bligh Reef in Prince William Sound, Alaska producing the largest oil spill in U.S. history. Following this event, the Coast Guard reexamined its mission needs and technology to formulate an R&D effort for the 1990's. Workshops were held within the Coast Guard and with other Federal agencies and private sector organizations to identify spill response needs and R&D efforts that would support those needs. One of the workshops was a U.S. Coast Guard sponsored Interagency Planning Workshop on oil spill research and development on September 26-27, 1989. This workshop exchanged information and initiated the development of a coordinated national plan for oil spill research and development under Title VII of the Oil Pollution Act of 1990.

The Oil Pollution Research Grant Program was created by the Oil Pollution Act of 1990, P.L. 101-380 (OPA 90), 33 U.S.C. 2761 (c)(8) and 2761 (c)(9). The OPA established a regional research program and authorized those agencies represented on the Interagency Coordinating Committee on Oil Pollution Research, including the U.S. Coast Guard (USCG), to make grants to universities and other research institutions to perform research related to regional effects of oil pollution. The USCG established such a grant program, and the Volpe National Transportation Systems Center (Volpe Center), a component of the Research and Special Programs Administration of the Department of Transportation (DOT), was chosen to administer this program on behalf of the USCG.

The Volpe Center mailed Grant Applications to about 145 universities and non-profit research institutions on December 21, 1993. The mailing list included institutions from all the Coast Guard regions. On March 7, 1994 the Volpe Center received 14 applications from four regions. These proposals were reviewed by the Volpe Center and the Coast Guard Research and Development Center and the recommendations forwarded to the Interagency Committee on Oil Pollution Research for approval. Nine one year Grants were awarded in August 1994. Coast Guard funds were matched by funds from the university or non-profit research institution.

This report contains the Final Reports for research performed under these Grants. The results are presented in two volumes. For further information contact Kenneth Bitting at the U.S. Coast Guard Research and Development Center, Groton, Conn. (860) 441-2733.

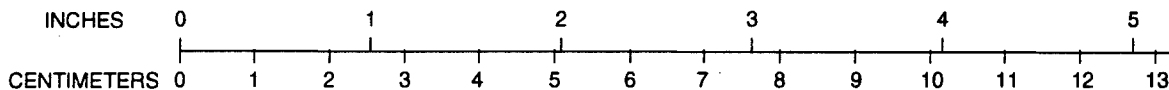
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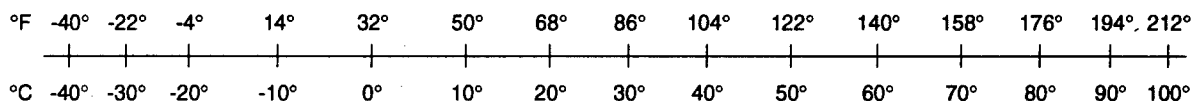
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<b>LENGTH (APPROXIMATE)</b> 1 inch (in) = 2.5 centimeters (cm) 1 foot (ft) = 30 centimeters (cm) 1 yard (yd) = 0.9 meter (m) 1 mile (mi) = 1.6 kilometers (km)	<b>LENGTH (APPROXIMATE)</b> 1 millimeter (mm) = 0.04 inch (in) 1 centimeter (cm) = 0.4 inch (in) 1 meter (m) = 3.3 feet (ft) 1 meter (m) = 1.1 yards (yd) 1 kilometer (km) = 0.6 mile (mi)
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<b>MASS - WEIGHT (APPROXIMATE)</b> 1 ounce (oz) = 28 grams (gm) 1 pound (lb) = .45 kilogram (kg) 1 short ton = 2,000 pounds (lb) = 0.9 tonne (t)	<b>MASS - WEIGHT (APPROXIMATE)</b> 1 gram (gm) = 0.036 ounce (oz) 1 kilogram (kg) = 2.2 pounds (lb) 1 tonne (t) = 1,000 kilograms (kg) = 1.1 short tons
<b>VOLUME (APPROXIMATE)</b> 1 teaspoon (tsp) = 5 milliliters (ml) 1 tablespoon (tbsp) = 15 milliliters (ml) 1 fluid ounce (fl oz) = 30 milliliters (ml) 1 cup (c) = 0.24 liter (l) 1 pint (pt) = 0.47 liter (l) 1 quart (qt) = 0.96 liter (l) 1 gallon (gal) = 3.8 liters (l) 1 cubic foot (cu ft, ft <sup>3</sup> ) = 0.03 cubic meter (m <sup>3</sup> ) 1 cubic yard (cu yd, yd <sup>3</sup> ) = 0.76 cubic meter (m <sup>3</sup> )	<b>VOLUME (APPROXIMATE)</b> 1 milliliter (ml) = 0.03 fluid ounce (fl oz) 1 liter (l) = 2.1 pints (pt) 1 liter (l) = 1.06 quarts (qt) 1 liter (l) = 0.26 gallon (gal) 1 cubic meter (m <sup>3</sup> ) = 36 cubic feet (cu ft, ft <sup>3</sup> ) 1 cubic meter (m <sup>3</sup> ) = 1.3 cubic yards (cu yd, yd <sup>3</sup> )
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**EFFECTS OF THE WATER ACCOMMODATED FRACTION OF CRUDE OIL AND  
DISPERSED OIL ON THE EARLY LIFE STAGES OF TWO MARINE SPECIES**

*Michael M. Singer, Ronald Tjeerdema, University of California*

## EXECUTIVE SUMMARY

The aim of UCSC's research program has been to attempt to bring a measure of standardization to the investigation of the acute toxicity of dispersants, oil, and their mixtures. Compilation of scientifically defensible, realistic, and easily comparable data, will allow direct assessment of different dispersants and their effects on the toxicity of various oils in a timely manner in the event of a spill. Our previous work was concerned with selection and validation of the different biological and analytical techniques to be used to establish standard test solution preparation and toxicity test methodologies for use with aquatic organisms using a test system developed and validated by our laboratory over the past eight years. In this U.S. Coast Guard co-funded phase of the program, methods for the preparation of water-accommodated fractions (WAFs) of oil, and chemically dispersed oil (CDO) were investigated, and flow-through, spiked-exposure toxicity tests with Prudhoe Bay crude were performed on the early life stages of two marine species.

After several months of methods development, a standard protocol was constructed for the consistent preparation of crude oil WAFs; this framework has been adopted by several other laboratories in the U.S. and Canada as a standard method in the hopes that more readily comparable data can be produced by different groups. Development of a similar standard protocol for preparing CDO solutions was initiated, and is still evolving.

WAF toxicity tests were conducted with the early life-stages of two marine species, the red abalone (*Haliotis rufescens*), and a kelp forest mysid (*Holmesimysis costata*). At oil loadings as high as 25 g/L, no significant effects were seen in terms of either abalone larval development or juvenile mysid mortality. However, significant effect was seen in mysids at loadings as low as 1 g/L in terms of a new narcosis endpoint. This narcotic endpoint may be an important tool in assessing toxic effects because even though it is reversible (most animals were seen to recover), it may represent a measure of "ecological death" with significant ramifications to natural populations.

Because of the protracted amount of time involved in WAF protocol development, only a single, preliminary CDO mysid test was performed during the grant period. Results of this test indicated that the chemical dispersion of oil resulted in toxic effects at significantly lower oil loadings. However, insufficient data exist to allow conjecture about the reasons for this difference (e.g. the presence of particulate oil, enhanced dissolved oil fractions, dispersant-related effects).

## INTRODUCTION

Surfactant-based oil spill cleanup agents (dispersants) have been used in response to marine spills worldwide for over 30 years. However, the earliest formulations, such as those used in the *Torrey Canyon* spill, were aromatic hydrocarbon-based products meant primarily for cleaning tanker holds, bilges, etc. (NRC 1989); these products turned out to be as toxic, if not more so, to marine life than the oil they were meant to clean up (Smith 1968). Stemming from these early problems, the primary concern surrounding dispersant use in the U.S. to date has been the generally held assumption that dispersants increase the toxicity of oil to marine organisms. If this assumption is indeed true, then dispersant use should be limited to very special circumstances; however, if not true, a potentially beneficial spill countermeasure is being removed from the response arsenal as a result of insufficiently determinate data. It is therefore important to compile sound, directly comparable scientific data on these chemicals and their effects both alone and in concert with oil.

Over the past two decades a fairly large body of scientific literature concerning the effects of dispersants, oil, and dispersant/oil mixtures on marine organisms has been produced in an attempt to address the above issue (reviews by Allen 1984, Rice 1985, Tjeerdema *et al.* 1989, NRC 1989, Smalheer *et al.* 1992, Markarian *et al.* 1995, among others). However, the wide variety of biological, chemical, and analytical methods employed has produced a diverse collection of data which does not easily lend itself to cross comparison. Even when differences in methodology, species, life stages, etc. are put aside, consistent conclusions are not readily forthcoming. A number of studies have concluded that dispersed oil elicits higher toxicity to marine organisms than oil or dispersants alone (e.g. Tarzwell 1971, Verriopoulos and Moraitiou-Apostolopoulou 1982, Bobra *et al.* 1989); however, in some cases, dispersant alone has been seen to be more toxic than either dispersed or undispersed oil (Unsal 1991). Increased toxicity of dispersed oil (chemically or mechanically) has been linked variously to particle size in the dispersion (Bobra *et al.* 1989), and on aromatic hydrocarbon content (especially mono- and diaromatics; Anderson *et al.* 1987). In truth, however, oil toxicity is brought about by a number of interacting chemical, physical, and physiological factors.

Large amounts of oil are moved through the nearshore marine waters of the United States daily, and the eventual likelihood of a significant accidental spill is high, thus the need for a wide variety of countermeasures at the disposal of response authorities is essential. In order to address concerns over inadequate preparedness by the state of California to effectively deal with a large oil spill, legislation was passed in 1987 to begin a research program to investigate fundamental regulatory and scientific questions regarding chemical oil spill cleanup agents. Over the past seven years a cooperative research effort sponsored by the California Department of Fish and Game's Office of Spill Prevention and Response (OSPR) and the University of California, Santa Cruz (UCSC), has addressed the question of oil spill cleanup agent toxicity using standardized methods and species. This research has involved the development of a new, state-of-the-art test system for use with the early life stages of marine species (Singer *et al.* 1990a, 1993), and straightforward, rapid analytical techniques.

Our exposure system and test methodology have become internationally recognized as representing the cutting edge of the technology. The system design has been presented at international toxicological meetings and has garnered interest by researchers in industry, government, and academia throughout North America and Europe. With the interest and support of the Marine Spill Response Corporation (MSRC), it is emerging as the standard technology for toxicity evaluation of oil spill cleanup agents nationwide; in an effort to set up a series of laboratories across the country all using the same (our) methods, duplicate systems purchased by MSRC, and fabricated by UCSC personnel, are now being used by Exxon Biomedical Sciences, Inc. (EBSI), and by state and/or academic institutions in Texas, Louisiana, and Florida. Our relationship with MSRC has resulted in widespread exposure for our methods throughout the oil spill response community. Toxicological data generated by

this program over the years have appeared in seven publications in international peer-reviewed journals and twelve presentations at scientific conferences by a number of key program personnel, as well as invited participation by the principal investigator in several international workshops and advisory groups in both the U.S. and Canada.

When used correctly, dispersants combine with oil in the field, thus the comparison of the toxicity of each alone to that of their mixture is of crucial importance when evaluating the utility of dispersant use. Therefore, an understanding of the effects of dispersants on natural oil toxicity is needed to provide guidance as to when their use may, or may not, be appropriate. Use of standardized test protocols and species will allow a more accurate comparison of toxicity between agents, oils, and agent-oil combinations. Ultimately, the benefit of standardized information will be realized by responsible on-scene personnel charged with deciding whether, and which, dispersants to use for oil spill response.

The current UCSC oil spill cleanup agent research program, which is currently jointly funded by OSPR, MSRC, the California Sea Grant Program, and the University of California Toxic Substances Research and Teaching Program is concerned with several important aspects of the regulatory and scientific questions surrounding the use of chemical cleanup agents. Our main areas of research are: 1) the acute toxicity of dispersants, oil, and their mixtures to marine organisms under standardized conditions, 2) evaluation of dispersant performance (efficacy) under standardized conditions, and 3) the biochemical fate of both dispersant and oil constituents in marine organisms. The first and second areas have immediate regulatory, as well as scientific, relevance in that by determining the relative differences in toxicity and efficacy between the various dispersants available, on-scene coordinators will have sound data on which to base response decisions, thereby allowing field personnel, equipment, and dollars to be used most efficiently.

The overall goal of the acute toxicity portion of UCSC's research program is to evaluate the effects of oil, dispersants, and their mixtures in order to assess whether and/or to what extent dispersants may influence the aquatic toxicity of oil, and how this effect may be altered by differing types of dispersants and oils. To achieve this end, the toxicity of dispersants alone were first evaluated using a suite of taxonomically and trophically diverse marine species. Five dispersants have so far been evaluated (Singer *et al.* 1991, 1993, 1994a, b, 1995). These data serve as a solid information base from which the current USCG co-funded program was launched, and also provide substantial validation for our toxicity test system and procedures. The next step, described in the present report, was to describe the toxicity of oil alone (water-accommodated fraction; WAF) under the same conditions, using the same procedures. These data can then be used as a frame of reference by which to evaluate the toxicity of dispersant/oil (D/O) mixtures. Comparison of the effects of oil alone and in combination with dispersants under relatively "realistic" exposure conditions can also provide insight into the ecological costs and benefits associated with dispersant use in spill situations.

The specific objectives addressed in this report included: 1) specification of standard preparation protocols for crude oil WAFs and chemically-mediated dispersions, 2) conducting declining-exposure toxicity tests with Prudhoe Bay crude oil WAF using juvenile mysids and larval abalone, and 3) conducting declining-exposure toxicity tests with Prudhoe Bay crude oil dispersed with Corexit 9527 using juvenile mysids and larval abalone.



## SPECIFICATION OF STANDARD TEST SOLUTION PREPARATION PROTOCOL FOR WATER-ACCOMMODATED FRACTIONS (WAFs) OF OIL

After preliminary methodological work, we found that specification of a standard WAF preparation protocol would require a longer time than was first envisioned. Early on we identified several factors important in the consistent preparation of WAFs. Among these were pretreatment of dilution water (filtration, sterilization, etc.), mixing energy, and mixing duration. Systematic investigation of the influences of each of these factors on the resulting solution have led to the specification of a draft version WAF preparation protocol, which is included here as Appendix 1.

It may be of some utility to define our use of the term WAF at this juncture, since more than one definition is possible. The goal of the methods described below was to achieve a reproducible, saturated, non-particulate solution derived from an oil/water mixture. Use of the term WAF, as opposed to water soluble fraction (WSF), may be preferable to satisfy the condition that a true WAF has been defined as only producible if steps were taken to ensure that all possible particulate oil was removed, such as filtration or centrifugation (Girling 1989, Bennett *et al.* 1990, Girling *et al.* 1992). These steps would make it necessary to physically handle the solution, possibly introducing an unwanted source of chemical loss, or change. Therefore, while the resultant procedures described here produce a solution verifiably free of emulsified oil (a WAF), we feel continued use of the term WAF is technically appropriate.

### Dilution Water Pretreatment

It was determined early on that toxicity testing in seawater was of primary concern to both UCSC and co-funding entities, and thus no attempt was made to include freshwater preparations. However, toxicity testing in various salinities may be of future interest in a number of cases. We have no direct data on the effect of different salinity dilution water on the resultant WAF. However, discussions with other investigators involved in similar research lead us to conclude that no significant operational changes in the herein presented protocol are necessary on the basis of salinity, when natural seawater is used as the basic medium.

Normal toxicity test seawater handling in our laboratory involves filtration to 1  $\mu\text{m}$  with activated carbon polishing. However, it was found that microwave treatment of this 1  $\mu\text{m}$  filtered seawater prior to WAF preparation yielded more consistent solutions (Singer and Tjeerdema 1995). This method of pretreatment was used throughout much of our preliminary work. At a meeting in March 1995 with other laboratories across North America embarking on similar WAF toxicity research, it became evident that for reasons of facilities, volumes, etc., most other participating laboratories were unwilling or unable to duplicate this procedure. A pretreatment method that was available to all laboratories was filtration, and it was decided that 0.45  $\mu\text{m}$  filtration would be investigated. Filtration to this small size has the operational cost of slowing water flow, however, this delay is significantly less than that associated with microwave treatment, in which water is heated and then must be cooled before use. Side-by-side preparation of WAFs using microwaved versus 0.45  $\mu\text{m}$  filtered seawater resulted in no significant difference in the final solutions (Fig. 1)

### Mixing Energy

All data cited herein were obtained with the use of electromagnetic stirring plates as the mixing energy source (Cole Parmer, Vernon Hills, IL; Singer and Tjeerdema, 1995). These stirrers were chosen for ease of use and reproducibility, and have several advantages over other forms of mixing. Although mixing energy for preparation of WAFs can be accomplished in a variety of ways (shaking, swirling, rotating, etc.), not all are amenable to use with large volumes (as much as 20 L for each treatment) for reasons of practicality and/or

Table 1. Summary of experimental conditions during mixing energy investigation.

Trial #	Oil Loading Rates (g/L)	Energy level
1	0.01, 0.1	vortexed
2	1, 10	vortexed
3	0.01, 0.1	nonvortexed
4	1, 10	nonvortexed

safety. Therefore, magnetic stirrers were chosen because they can be used with essentially any size vessel with little or no modification or construction of devices or holders. The use of electromagnetic stirrers provides a high level of repeatability and accuracy to the process because no moving parts are involved (as in traditional mechanically-driven stirrers, in which a magnet is spun by means of a motor) and thus will not experience wear over time. They also provide the added benefit of having digital rpm readouts, which preclude the necessity of purchasing a tachometer for stir rate verification (which must be done for each test). While these types of stirrers are more costly initially than mechanically-driven ones, we feel that their savings in manhours and ancillary equipment, along with their stability, are worth the expenditure, especially for laboratories that do not possess enough stirrers to begin testing.

Initial investigations into crude oil WAF preparation methods employed an energy level sufficient to achieve a 20-25% depth vortex in the mixing vessel (Anderson *et al.* 1974). Although this method produced no identifiable dispersion or emulsification with Prudhoe Bay crude in our trials, subsequent discussions with other researchers in the field indicated that this energy level may be too high when used with other oil types. Therefore, a lower energy method, in which no vortex was produced was investigated. This decision makes these procedures applicable to a wide range of oils and refined products having varying emulsion-forming tendencies.

To investigate the effect of energy level on the resulting WAFs, two sets of solutions were produced side-by-side, one with a vortex, and one without. Data were generated in four separate trials. In all, four loading rates (ratio of oil to water, expressed as mass per volume) were used; 0.01, 0.1, 1, and 10 g/L. In each trial, triplicate aspirator bottles were prepared at each of two loadings, all at the same mixing energy level (Table 1). In the vortexed trials, samples were spun at an energy level sufficient to achieve a 20-25% vortex for 18 h. It is important to note here that this amount of energy was dependent upon the amount of oil in the sample (i.e. the oil/water ratio); generally, larger amounts of oil (high loadings) needed less energy to achieve their vortex than did low loadings (Table 2). In nonvortexed trials all samples were spun for 24 h at a standard energy level in which no vortex was formed at any loading. This standard spin rate was comparable to that used by Environment Canada in parallel efforts (Blenkinsopp 1994). No settling time was found to be needed in any of the trials, as no dispersion or emulsion was apparent.

After mixing was complete, two sets of chemical analyses were performed on all samples. First, each sample was measured for total carbon (TC) content by high-temperature combustion. Second, a 15 mL aliquot of all samples was extracted with dichloromethane (DCM) and analyzed by flame ionization gas chromatography (GC/FID); chromatograms were assessed for both qualitative and quantitative differences between the two energies.

We found that the nonvortexed method of mixing resulted in the use of comparable energy levels among widely different loadings with much less variability than the vortexed method (Table 2). Results of TC analysis showed no significant difference in the final solutions derived from the 1 and 10 g/L loadings, however the TC concentrations of the two lower loading rate solutions were statistically different (Fig. 2). GC-derived total

Table 2. Summary of mixing energies employed in WAF preparation (n=3).

Loading Rate (g/L)	Mean Spin Rate in rpm (%SD)	
	Vortexed	Nonvortexed
0.01	445.3 (3.7)	197.3 (0.8)
0.1	407.3 (3.5)	199.3 (0.6)
1	412.3 (2.7)	194.3 (0.6)
10	260.7 (2.2)	196.7 (0.6)

hydrocarbon data, however, indicated no difference at either 0.01, 0.1, or 1 g/L, with only the 10 g/L samples being statistically different (Fig. 3). It should be noted here that no chromatographic evidence (e.g. the presence of an *n*-alkane series) of the presence of particulate oil was seen in either the vortexed or nonvortexed samples.

From these data, we have concluded that in the majority of cases, we would expect the nonvortexed method to provide reproducible solutions appropriate for toxicity testing purposes. Data generated in Canada with other oils in different size vessels have led to a similar conclusion (Blenkinsopp 1994).

### Mixing Duration

Having established mixing source and method, it was necessary to establish a mixing duration necessary to achieve saturation of the available soluble compounds in a variety of loading amounts. This investigation involved two trials with two loadings each with each loading replicated three times; the first trial consisted of 0.01 and 0.1 g/L loadings, and the second of 1 and 10 g/L loadings. Each replicate was sampled for TC analysis at various time intervals, up to 72 h (Fig. 4). In addition, one replicate of each loading was sampled at 24, 48, and 72 h for total hydrocarbon analysis (Fig. 5). All samples in this investigation were spun at  $200 \pm 10$  rpm (nonvortexed).

In the 0.01 and 0.1 g/L loadings, TC data showed no further increase (within statistical variability) after about 6 h of spinning. In the two higher loadings, TC data were seen to cease increasing after 24 h, again within statistical variability (Fig. 4). GC hydrocarbon content data showed no substantial difference between 24 and 72 h samples in the 0.01, 0.1, and 1 g/L loadings, supporting the conclusion of saturation derived from TC data. However, GC data showed a continual increase through 72 h, in contradiction to TC data (Fig. 5). Similar high loading rate data have been generated by Environment Canada to differing extents with different oils (Blenkinsopp 1994). Thus, it appears that minimum mixing time may have to be extended for some oils at some loadings, and that this condition will have to be assessed for each oil or oil product on an individual basis.

### Mixing Vessel Size

There exists a wide variety of toxicity test protocols, each demanding different amounts of test solution. Therefore, it is reasonable to assume that a variety of mixing vessel sizes will be called for by different laboratories. Discussions with researchers from the two other laboratories currently involved with similar studies, EBSI and Environment Canada, revealed wide differences in the size of vessels used to generate WAFs for toxicity testing. Our laboratory employs 2 L (nominal) glass aspirator bottles, whereas Environment Canada employs 20 L flourinated nalgene carboys, and EBSI uses 2, 4, 8, and 13 L glass aspirator bottles. Clearly, a comparison of vessel geometries was necessary, as well as a comparison of

Table 3. Comparison of physical parameters of various size WAF preparation vessels.

Nominal Vessel Size	Current Users	Material	Actual Water Volume Used (L)	Headspace Volume (L)	Surface Area/Volume Ratio	% Headspace
2 L	UCSC/ EBSI	Glass	1.8	0.5	0.063	22.7
4 L	EBSI	Glass	3.5	1.0	0.053	22.2
8 L	EBSI	Glass	7.0	1.9	0.040	21.2
13 L	EBSI	Glass	12.0	1.1	0.032	8.7
20 L	Env. Can.	FHDPE <sup>1</sup>	20.0	5.0	0.032	20.0

<sup>1</sup> Fluorinated high-density polyethylene.

WAF attributes derived from these various sized vessels.

Data generated by Environment Canada on Alaskan North Slope (Prudhoe Bay) crude were generously furnished to us for comparison by Dr. S. Blenkinsopp and P. Boileau. The Canadian data, based on BTEX concentrations, showed virtually the same patterns as our investigations; i.e. at loadings of  $\leq 1$  g/L, saturation was attained in approximately 24 h, but complete saturation at higher loadings may require more time. Their data showed that chemical concentrations of 10 g/L loading solutions slowed their rate of increase continually after 24 h, indicating that saturation was being approached. This positive comparison was a favorable result, since these data represented the largest and smallest vessels used among the laboratories.

In order to compare the geometry of the various sized vessels being used, data were provided by both Environment Canada and EBSI (courtesy of J. Clark and G. Bragin) on height, diameter, volume, etc. of each vessel type. The parameters deemed to be of most significance were amount of headspace, and surface area to volume ratio. All comparative data were assumed to represent conditions in which the surface of the test solution was as high as possible, but still below the shoulder of the vessel.

Interestingly, with the exception of the 13 L bottles used by EBSI, headspace volume as a percentage of vessel volume was very consistent throughout a 10-fold variation in size, ranging from 20 to 22.7% (Table 3). The relationship of solution surface area to volume was seen to be very linear, with a regression coefficient of 0.9939 (Fig. 6). The numerical ratio of surface area to test volume ranged from .032 to .063 between the largest and smallest vessels (Table 3). However, since these extremes represented vessels which had already been seen to generate favorably comparative data, this difference was deemed negligible.

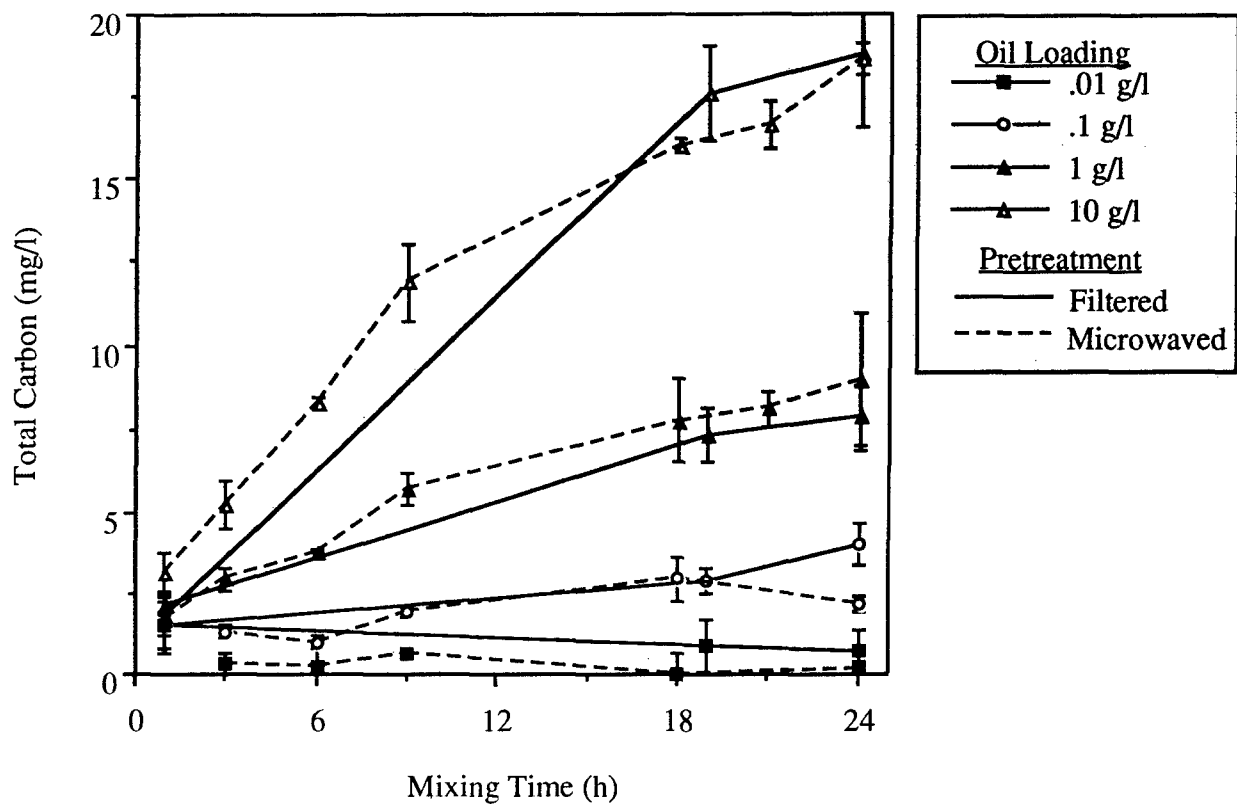


Figure 1. Comparison of total carbon concentrations in WAFs prepared with microwave sterilized versus 0.45  $\mu\text{m}$  filtered natural seawater. Data points represent mean  $\pm$  SD ( $n = 3$ ).

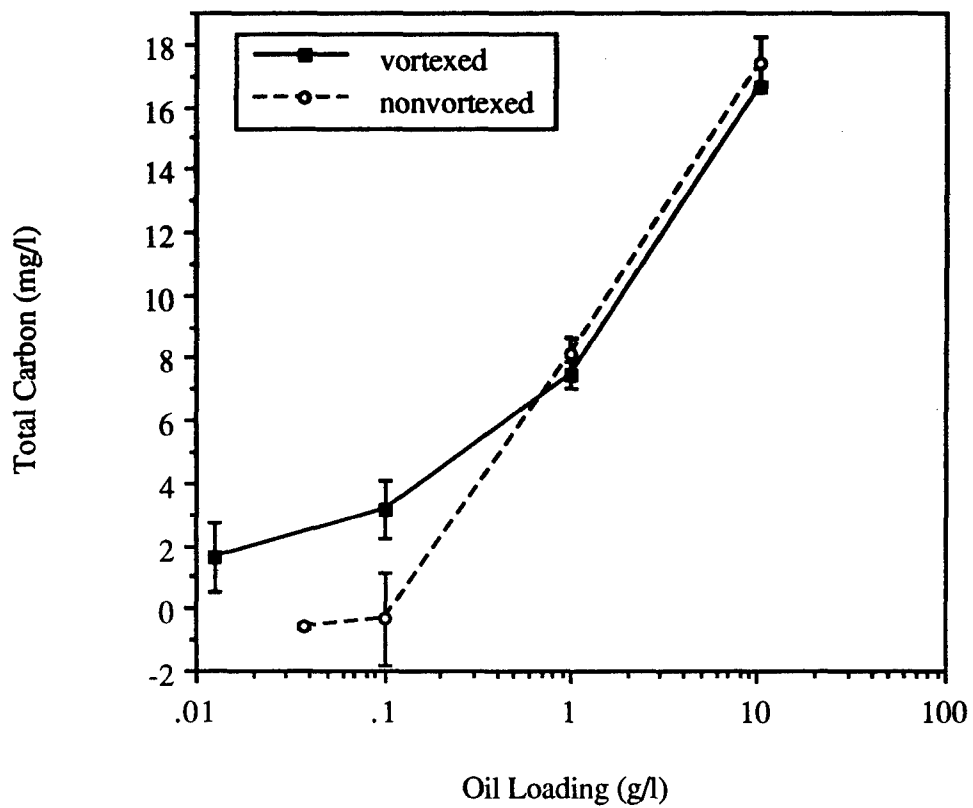


Figure 2. Comparison of total carbon concentrations in WAFs prepared at two different energy levels. Data points represent mean  $\pm$  SD ( $n = 3$ ).

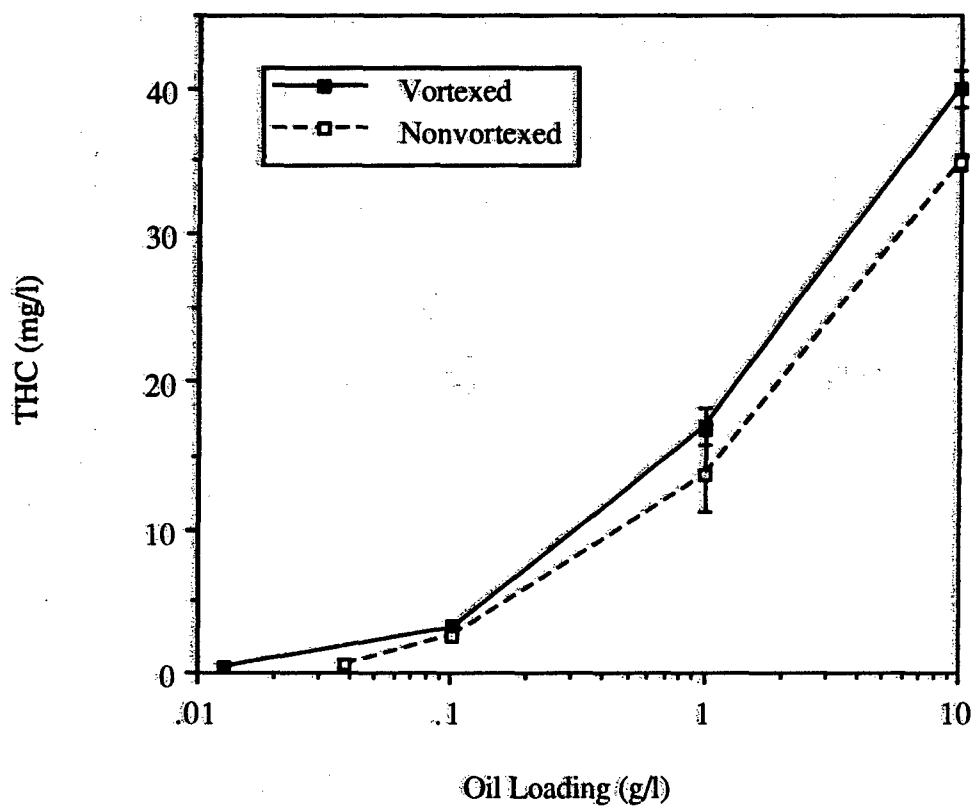


Figure 3. Comparison of GC/FID-derived THC concentrations in WAFs prepared at two different energy levels. Data points represent mean  $\pm$  SD ( $n = 3$ ).

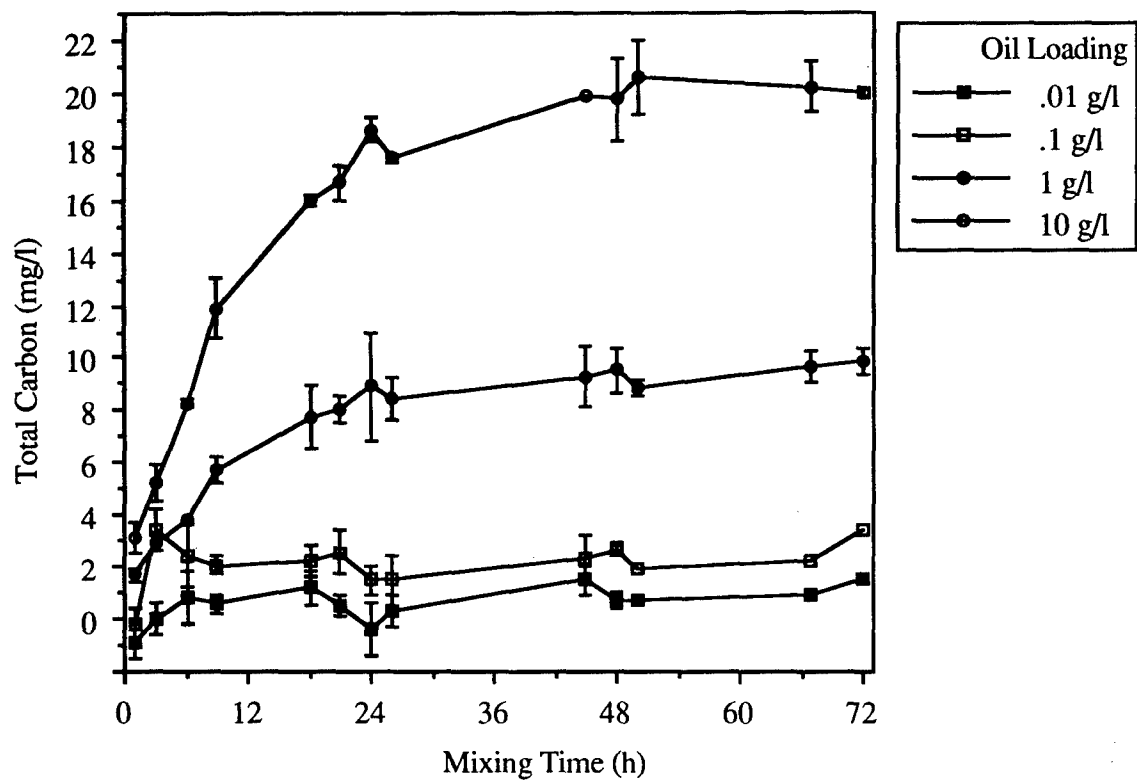


Figure 4. Determination of mixing time necessary to reach stability at various oil loadings. Data points represent mean  $\pm$  SD ( $n = 3$ ).



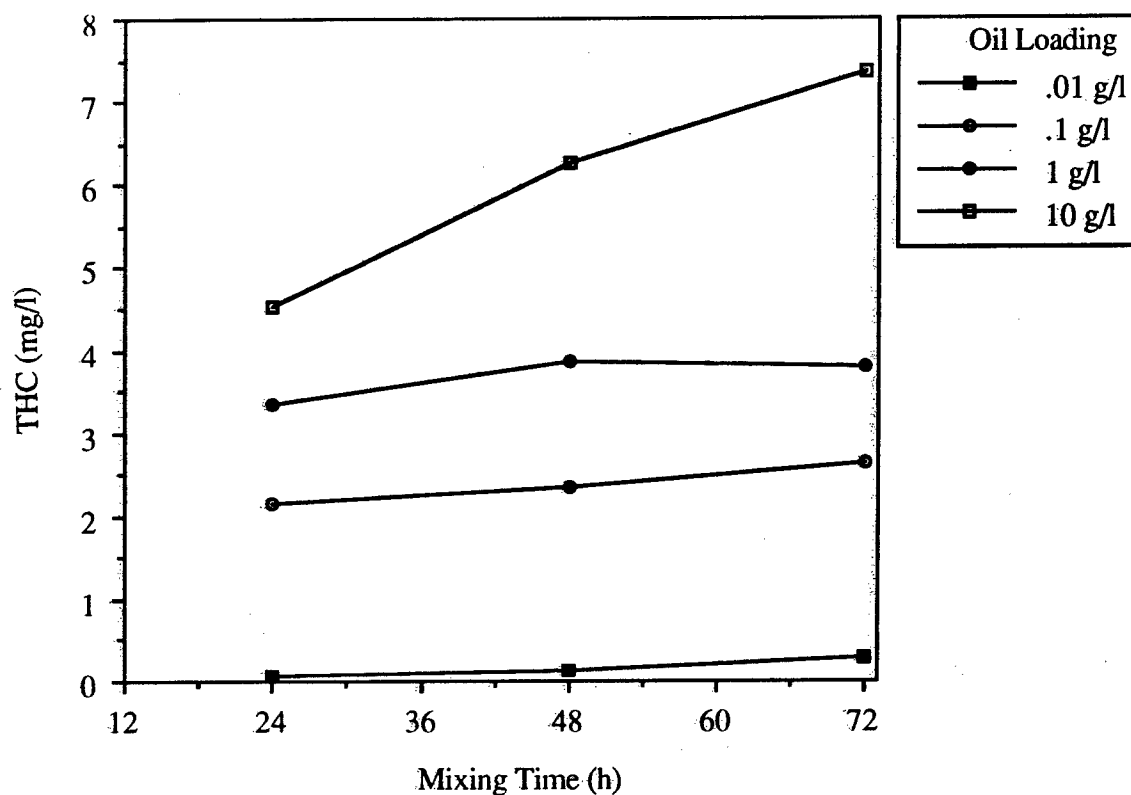


Figure 5. THC concentrations of WAFs after various mixing times ( $n = 1$ ).

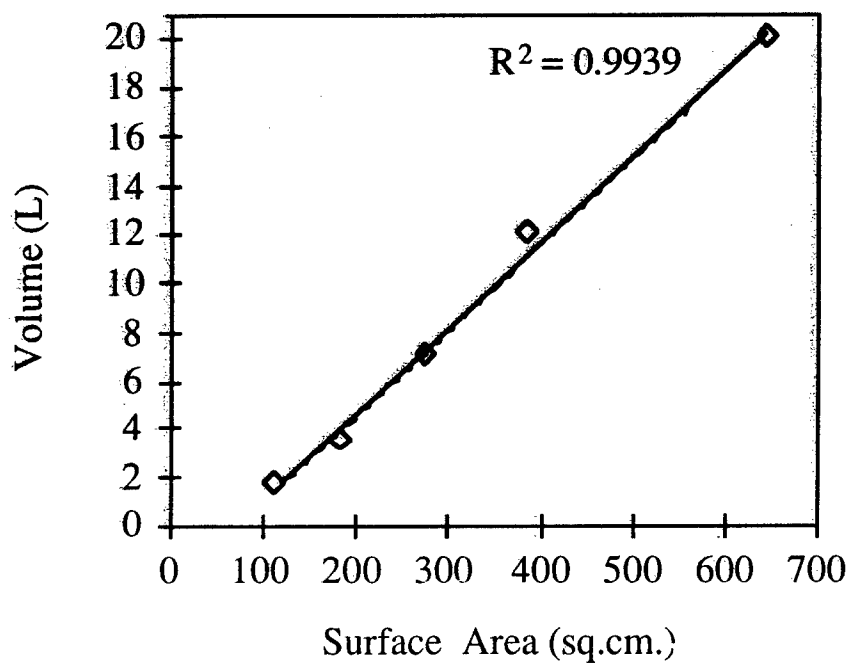


Figure 6. Relationship of WAF surface area to volume for different size vessels.

## **SPECIFICATION OF STANDARD TEST SOLUTION PREPARATION PROTOCOL FOR CHEMICALLY DISPERSED OIL (CDO)**

As with WAFs, it is of extreme importance that chemically dispersed oil solutions used for toxicity testing be prepared using standardized, repeatable conditions. To this end, after searching the literature for a consistent method, and finding none, development of an appropriate method that would yield quantitatively reproducible solutions was begun. It was decided to use the method currently employed at EBSI as a starting point. This method had the advantage that it was very similar to the method used for producing WAFs (e.g. mixing vessel, energy type, volume); oil was layered onto water, then a vortex was created on a magnetic stirrer, and then dispersant was added to the surface of the oil in the area of the vortex. After using this method to generate several CDO solutions, several parameters were seen as being potentially influential on the final product, including dispersant delivery method, energy level, sequence of events (oil addition, energy initiation, etc.), mixing duration, and settling time. In order to make WAF and CDO preparations similar, the same aspirator bottles, magnetic stirrers, stir bars, and water volumes were used in this phase of the investigation.

### **Dispersant Delivery Method**

This parameter can have a significant affect on the final solution, in that the degree of dispersion is dependent on the efficiency of contact between oil and dispersant. The most widely used method for adding dispersant is with a syringe, either dropwise or in a stream. A better method would be to employ some type of atomizer, simulating the jet-nozzled delivery devices used in field applications. However, after consultation with investigators at other laboratories, it was agreed that no device was readily available that could deliver a quantifiable mist that could be calibrated to field droplet size guidelines. Therefore, while arguably less than ideal, delivery by syringe was identified as the most practical and reproducible dispersant delivery tool.

### **Event Sequence**

Before other parameters such as mixing duration, settling time, etc. could be investigated, we found it necessary to define an optimum procedure for the actual delivery of oil and dispersant and initiation of mixing. In early trials oil was first added to a still water mass, then mixing was begun until a 25% vortex was achieved, at which time dispersant was added to the swirling oil slick at the vortex. This is the method employed at EBSI, and was designated the "standard" method for comparative purposes. This method had two fundamental shortcomings; 1) during the time that the vortex was being initiated (at least 30 s to 1 min) the oil was being spread over the entire water surface (usually in an uneven pattern), and 2) different amounts of energy were needed to create a standard 25% vortex at different oil loadings. The significance of the former is that at low loadings, as the available oil is spread, the likelihood of sufficient dispersant contact is greatly reduced. Also, the closer the oil is to the water/glass interface, the greater the chance of having oil thrown onto the walls of the aspirator bottle. The significance of the latter is that we have found that dispersion concentration is directly related to mixing energy, therefore, an extra source of variation in final solution concentration is introduced which cannot be controlled for.

Two other methods were initially investigated; one in which a 25% vortex was initiated in the water mass first, then oil and dispersant were both delivered into the vortex sequentially ("modified" method), and one in which both oil and dispersant were added from the same syringe simultaneously into an already vortexed water mass (single-syringe method). The single-syringe method was hypothesized to give the greatest potential contact by virtue of premixing inside the syringe prior to delivery.

In the first method comparison trial, the single-syringe method was seen to be inadequate. Regardless of which material was drawn into the syringe first, no mixing of oil and dispersant took place, and the dispersant was always delivered first, creating the unacceptable situation of adding oil to a dispersant/water mixture. Therefore, subsequent trials compared only the standard and modified two-syringe methods.

The two methods produced dispersions that behaved similarly in the next comparison test, but resulting solutions had different absolute concentrations. In this trial four replicates of each method were prepared at 1 g/L loading (10:1 O:D ratio). Dispersions were spun for 24 h and allowed to settle for 24 h. Solutions were quantified on the basis of total carbon content (TC). Results showed similar time/concentration behavior in the two methods, but with the modified method producing significantly higher concentrations at all but the last time point (Fig. 7). Unfortunately, 24 h of settling is of little practicality in terms of a toxicity test, because of oil weathering, etc. associated with such a long period. Further review of the data showed that the concentration differences seen were likely the result of different energy levels employed; standard method bottles required 330.0 ( $\pm 10.8$ ) rpm to achieve the proper vortex, but modified method bottles required 421.3 ( $\pm 5.2$ ) rpm to achieve a vortex without oil present.

This experiment was repeated (again at 1 g/L loading) using equivalent energy levels and results showed the two methods to produce essentially equivalent solutions (Fig. 8). Also, no significant difference in oil droplet density was seen between the two methods. Thus, there appeared to be no significant improvement associated with the modified method.

Since 1 g/L oil loading was surmised to be at the upper limit of most foreseeable toxicity tests, we felt it necessary to conduct a fourth method comparison test at a lower loading rate. This comparison was performed at a loading of 0.1 g/L. The most significant result of this test was the observation that using the standard method, only one of the four replicates dispersed to any degree, whereas all four of the modified method replicates exhibited good dispersion (Fig. 9). In this case, the spreading of the oil during vortex formation in the standard method replicates led to insufficient contact, and lower reliability.

From these data, we have concluded that use of the modified (prevortexed) method of making dispersions is preferred, and intend to use this method in further CDO work. The remaining parameters of interest, namely optimum mixing and settling times, will be investigated in future experiments.

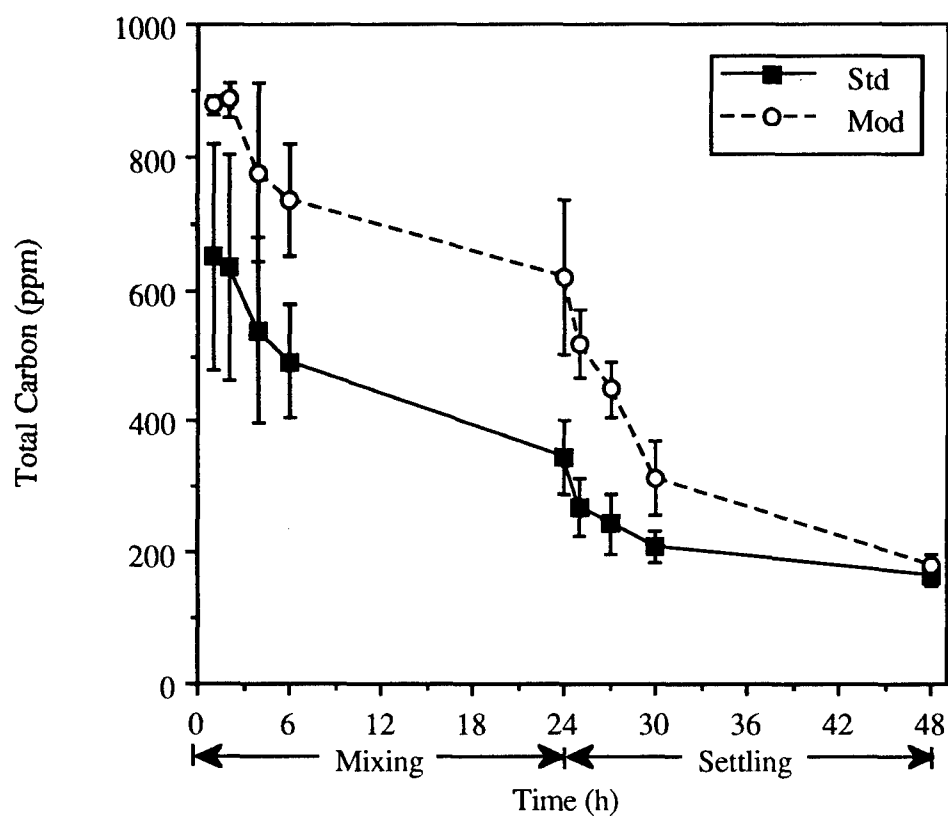


Figure 7. Initial comparison of standard (Std) and modified (Mod) methods of preparing 1 g/L oil loading chemical dispersions on the basis of total carbon concentration. Data are mean  $\pm$  SD ( $n = 3$ ).

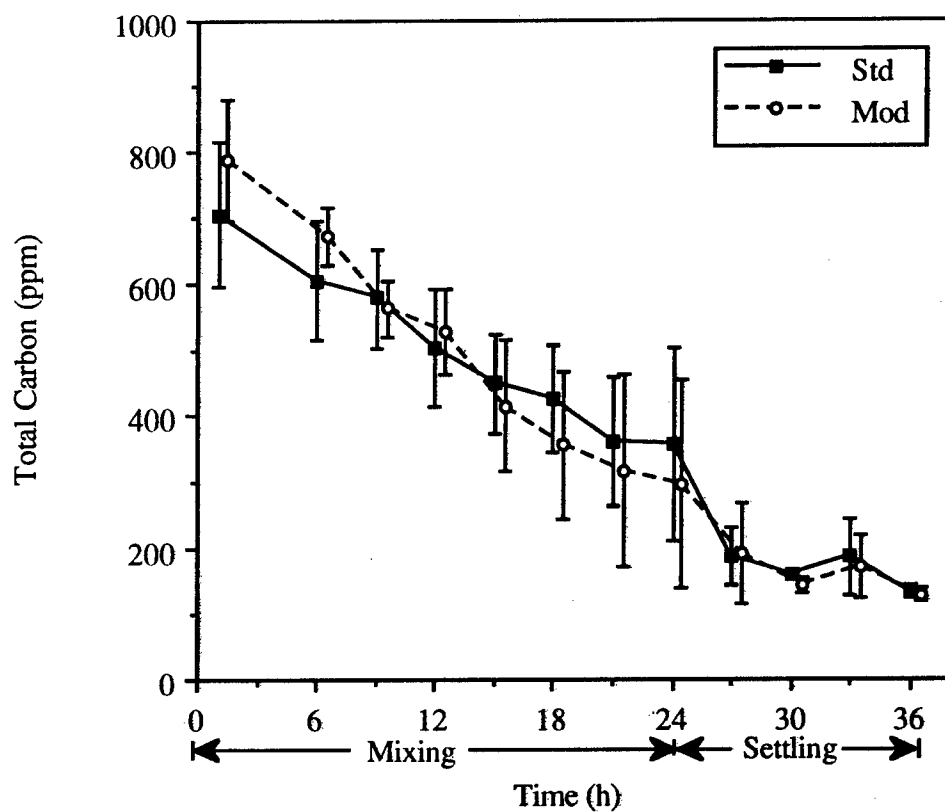


Figure 8. Comparison of standard (Std) and modified (Mod) methods of preparing 1 g/L oil loading chemical dispersions using equivalent mixing energies. Data are mean  $\pm$  SD ( $n = 4$ ); sampling periods equivalent between methods, but modified method data are offset for clarity.

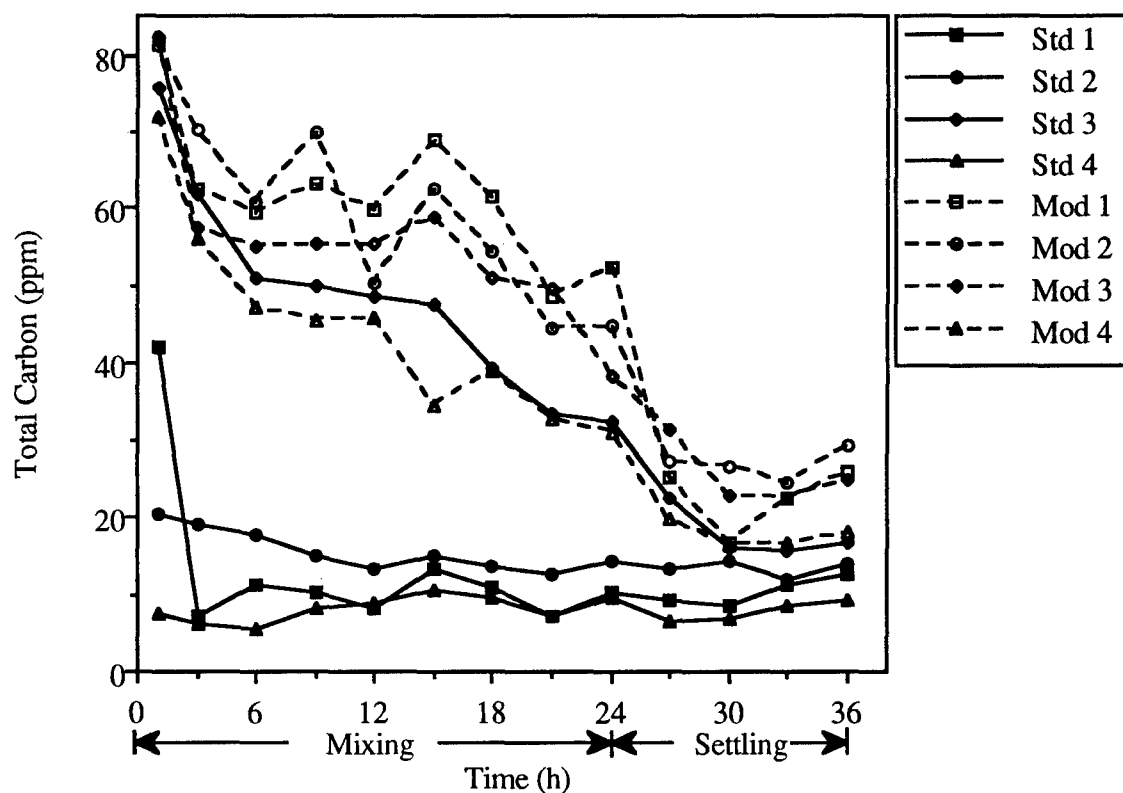


Figure 9. Individual replicate bottle total carbon concentrations in 0.1 g/L oil loading chemical dispersions using standard (Std) and modified (Mod) preparation methods.

## ANALYTICAL METHODS

To date, a number of WAFs have been prepared for use in toxicity tests using the protocol described in Appendix 1. Below are brief descriptions of our analytical procedures, as well as the analytical characteristics of these solutions.

### Gas Chromatography

Chromatographic analysis was accomplished using a Hewlett Packard 5890A Gas Chromatograph fitted with a flame ionization detector (FID). All samples for chromatographic analysis (GC/FID) were prepared by a liquid-liquid extraction method using dichloromethane (DCM) as the solvent. This procedure involved 15 mL of WAF being extracted three times with 3 mL DCM each time in a 125 mL separatory funnel on a wrist-action shaker. After each extraction, the solvent phase was collected into a 10 mL graduate, with the combined final extract volume made up to 10 mL. Extracts were stored in the freezer until analysis, at which time an aliquot was transferred to a 2 mL screw-cap GC vial with a teflon septum.

Whole oil dissolved directly into DCM was used as a standard for quantitation of WAFs. At least five oil standard concentrations were measured with each set of samples; standards were prepared by dissolving a known amount of oil into DCM gravimetrically, then serially diluting this "stock" with DCM directly into GC vials. Instrument parameters for chromatographic analysis were optimized to give maximum practical resolution in the range of compounds present in our WAFs (Table 4). Chemically dispersed oil was analyzed with the same instrument parameters as whole oil standards.

### Total Carbon Analysis

Total carbon concentration analysis (TC) was employed as a second analytical tool in this investigation. This type of analysis was selected because it involves a very short analysis time per sample (3–5 min), it requires only minute amounts of sample (50  $\mu$ L), and it does not require any sample preparation. In this technique, raw sample is injected directly into a 680°C furnace, where it is combusted and all available carbon is oxidized in the presence of a platinum catalyst into CO<sub>2</sub>, which is quantified by infrared absorption; all samples were analyzed using a Rosemount-Dohrmann DC-190 TOC Analyzer (Santa Clara, CA). While this technique cannot provide detailed fractional information, as chromatographic analysis can, it has great utility in tracking overall test solution concentrations during the initial exposure phase of toxicity tests (Singer and Tjeerdema 1995). In order to minimize loss of the lowest boiling-point fractions, TC samples were collected with an airtight syringe directly from each chamber through the teflon septum and analyzed immediately.

### Dispersion Droplet Size Analysis

Oil droplet size distribution and density are critical parameters in characterizing oil/water dispersions. The measurement of dispersed oil droplets has been accomplished in many ways, including photomicrography, Coulter counters, laser particle counters, and so on. Lacking access to more sophisticated (and expensive) equipment, we employed photomicrography as a means of analyzing droplet size and density. Samples for analysis were prepared as described by Payne *et al.* (1989); onto a standard glass microscope slide were placed 2 glass cover slips ( $\approx$  0.13 mm thick) approx. 15 mm apart, a 2  $\mu$ L drop of sample was placed between them, and was then capped by a third cover slip (Fig. 10). The "capping" cover slip provided a flat focal plane of reference for photography (photographs were taken at 100x magnification). Once developed, photos were projected onto a 5 x 5 cell

Table 4. Instrument parameters used in chromatographic analysis of WAFs.

Parameter	WAF Samples	Whole Oil Standards
Instrument	HP 5890A / 7673A Autosampler	
Column		
type	DB-5 glass capillary	
dimensions	60 m x .25 mm ID	
film thickness	.25 $\mu$ m	
Injector		
mode	split/splitless	
temperature	250°C	
volume	2 $\mu$ l	
Oven Temperature		
initial	29°C	29°C
ramp rates	10°/min to 150°, held 1 min 6.5°/min to 280°, held 5 min	10°/min to 150°, held 1 min 6.5°/min to 280°, held 5 min 10°/min to 325°, held 18 min
Detector		
type	Flame Ionization Detector	
temperature	325°C	

grid, and all droplets were measured in each of five randomly selected grids using a stage micrometer scale photographed for reference.

### Analytical Results

#### WAFs

Qualitatively, the WAF obtained from Prudhoe Bay crude oil was dominated by the BTEX fraction (benzene, toluene, ethylbenzene, xylenes) with smaller quantities of several alkylated benzenes, naphthalene, and the methylnaphthalenes also being present in quantifiable amounts (Fig. 11). No higher molecular weight compounds were found in identifiable quantities in these solutions.

Compositional comparison of WAFs derived from a range of oil loadings revealed that the major constituents did not increase proportionately with increased loading (Fig. 12). Even though each of the BTEX components increased in absolute amount with increased loading, the rates of increase for each component was different, and the relative proportions of these compounds to each other were not constant. These data, therefore, suggest that serial dilution of a high oil loading solution is not an appropriate substitute for preparation of a series of solutions derived from different loadings.

When initial WAF test solutions were quantified on the basis of total hydrocarbon content (THC) derived from whole oil chromatographic response, concentrations were seen to increase logarithmically in relation to oil loading (Fig. 13). In both abalone and mysid toxicity test solutions, THC concentrations increased asymptotically up to about 10 g/L loading, after which no substantial increase in concentration was seen. These data suggest that at loadings above about 10 g/L the solvent capacity of the water volume used has been



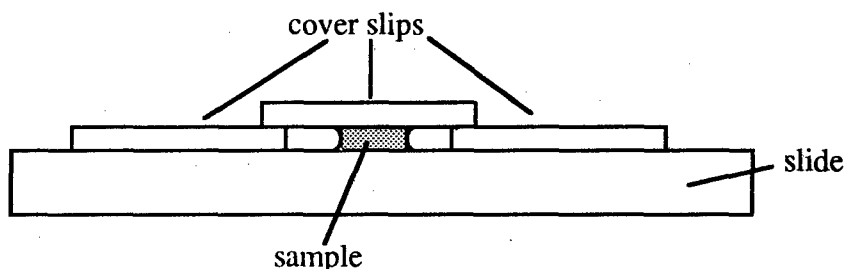


Figure 10. Schematic diagram of sample preparation setup for oil droplet size analysis photomicrography (not to scale).

reached. Similarly, when THC concentration was expressed as a percentage of the original oil that dissolved, a continually decreasing trend was seen, showing that given seawater's finite solvent capacity, increased loading simply resulted in a decreasing percentage dissolved (Fig. 14).

TC analysis was employed in parallel with gas chromatography on all initial test solutions. Trends in TC concentrations with increased loading were fundamentally similar to those seen with THC concentrations (Fig. 15). However initial TC values in two of the abalone tests showed little difference among the variously loaded WAFs.

The utility of using TC concentrations as estimators of THC concentration was also investigated. In mysid test solutions, THC was relatively linearly related to TC (regression coefficients ranged from .842 to .992; Fig. 16). However, this relationship was not seen in abalone test solutions, possibly resulting from the fact that in 4 of the 5 test loadings in these tests, both TC and THC had already begun to level off (Figs. 13, 15); regression coefficients for these data ranged from .367 to .758.

### *Chemical Dispersions*

Only one chemically dispersed oil toxicity test was conducted during this phase of the program. Analytical data on this test's initial solutions showed both THC and TC concentrations increasing logarithmically with increased oil loading over a fairly narrow range, 0.1 to 1 g/L (Fig. 17). Since THC concentration of chemical dispersions is likely heavily dominated by hydrocarbons derived from particulate (nondissolved) oil, it does not seem surprising that THC and TC concentrations were well correlated, with a regression coefficient of .977 (Fig. 18).

Oil droplet density data showed that at 1 g/L oil loading, there was, again, no significant difference in the two methods. Patterns of density versus time were similar, as were variability, which ranged from 20 to 60% for both methods (Fig. 19). The high variability seen in these data is likely the result of both relatively high heterogeneity of droplets in each sample, and too few samples; only two photographs of a single 2  $\mu$ L sample from each replicate were photographed. Operator subjectivity (consistent identification of oil droplets) was not deemed a significant factor in these data, as cross-checked samples by both readers gave very similar results. The overall pattern of droplet density with time was an approximate 50% increase in droplet density in the first 9 h of mixing, followed by an equally rapid decrease in density through the next 9 h of mixing. Densities remained relatively stable through the final 6 h of mixing (24 h total), and the first 3 h of settling, then were seen to rise substantially over the next 6 h of settling. No clear explanation has been found for this increase in droplet density after several hours of settling. Unfortunately, droplet size data were deemed unreliable because of high within- and between-operator

variability; in other words, actually measuring droplets proved to be much more difficult and inconsistent than simply identifying them. We feel that this photomicrographic technique could be better refined with the use of UV-fluorescence (UV/F) microscopy, if the equipment becomes available. UV/F microscopy allows for more reliable identification of oil droplets (versus other particles of air bubbles), and also provides better clarity of droplet boundaries used for measuring.

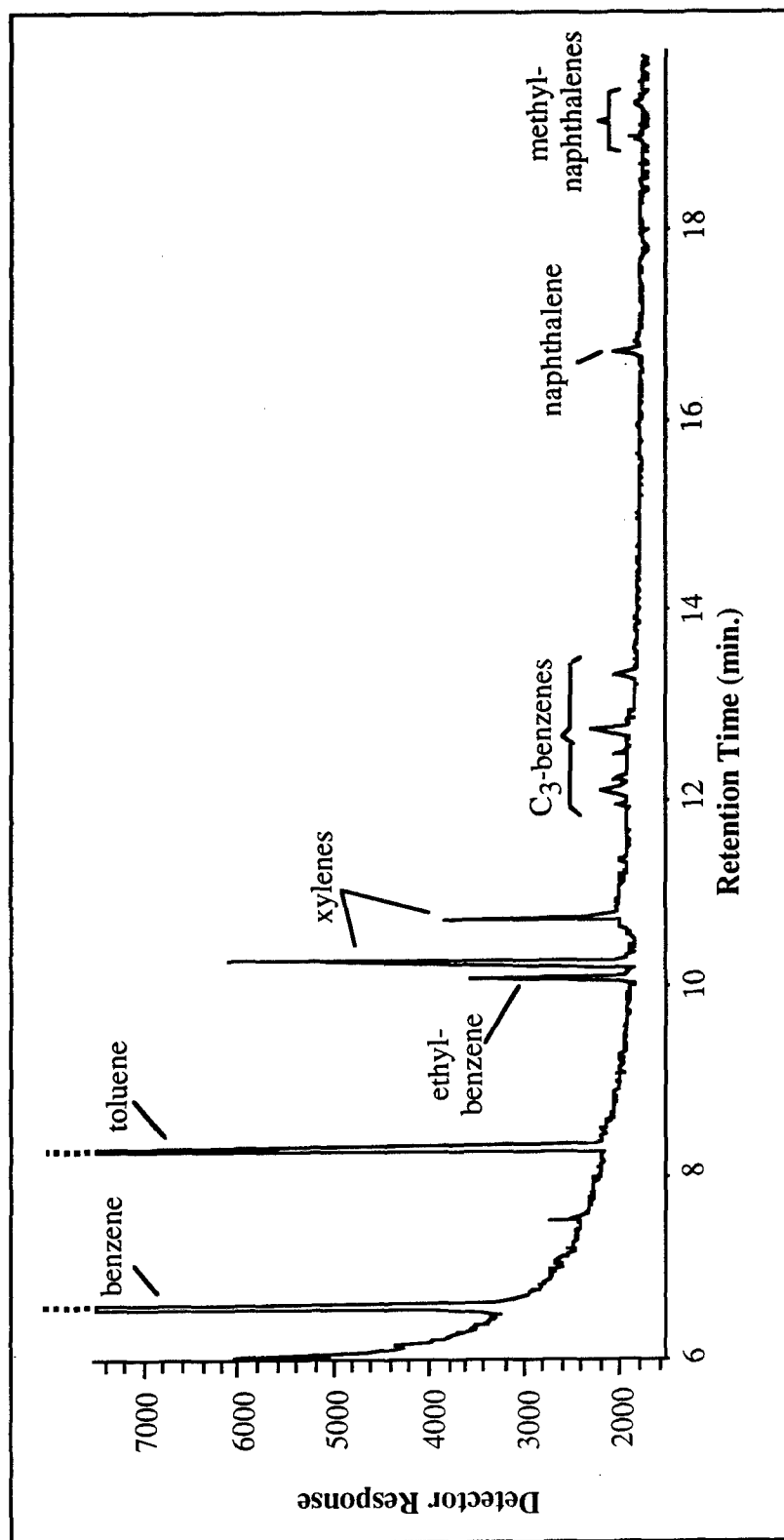


Figure 11. Representative GC/FID chromatogram of Prudhoe Bay crude oil WAF (note that benzene and toluene peaks are off-scale).

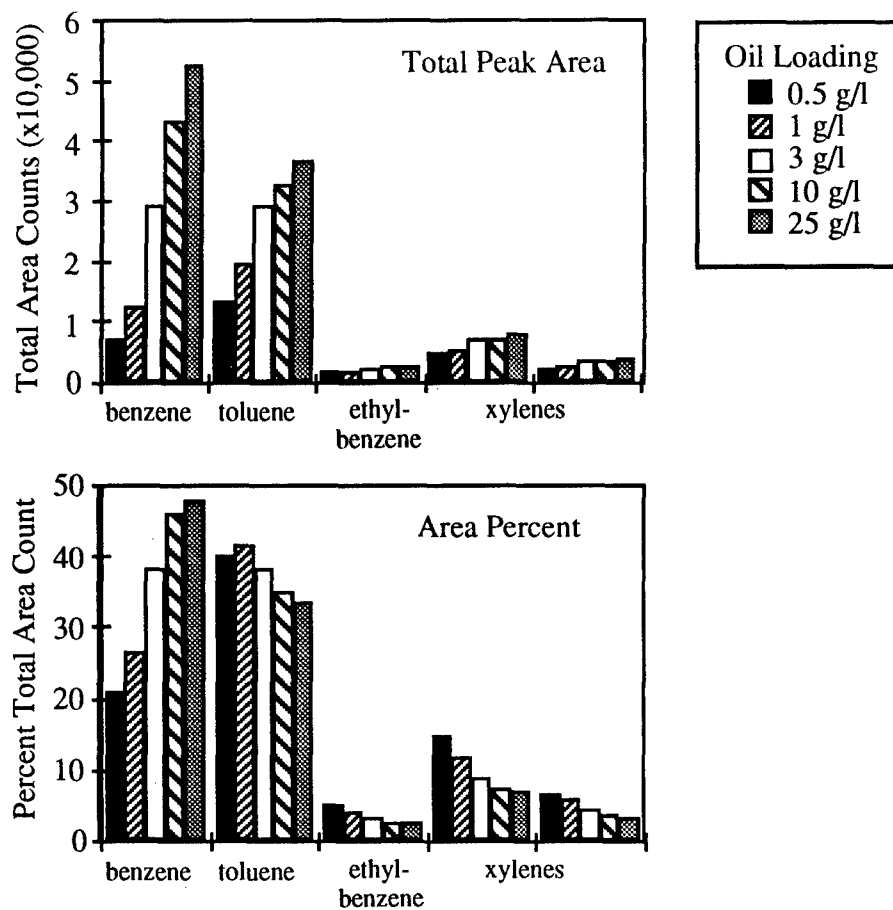


Figure 12. Absolute and proportional changes in BTEX fractions of Prudhoe Bay crude oil WAF at various oil loadings.

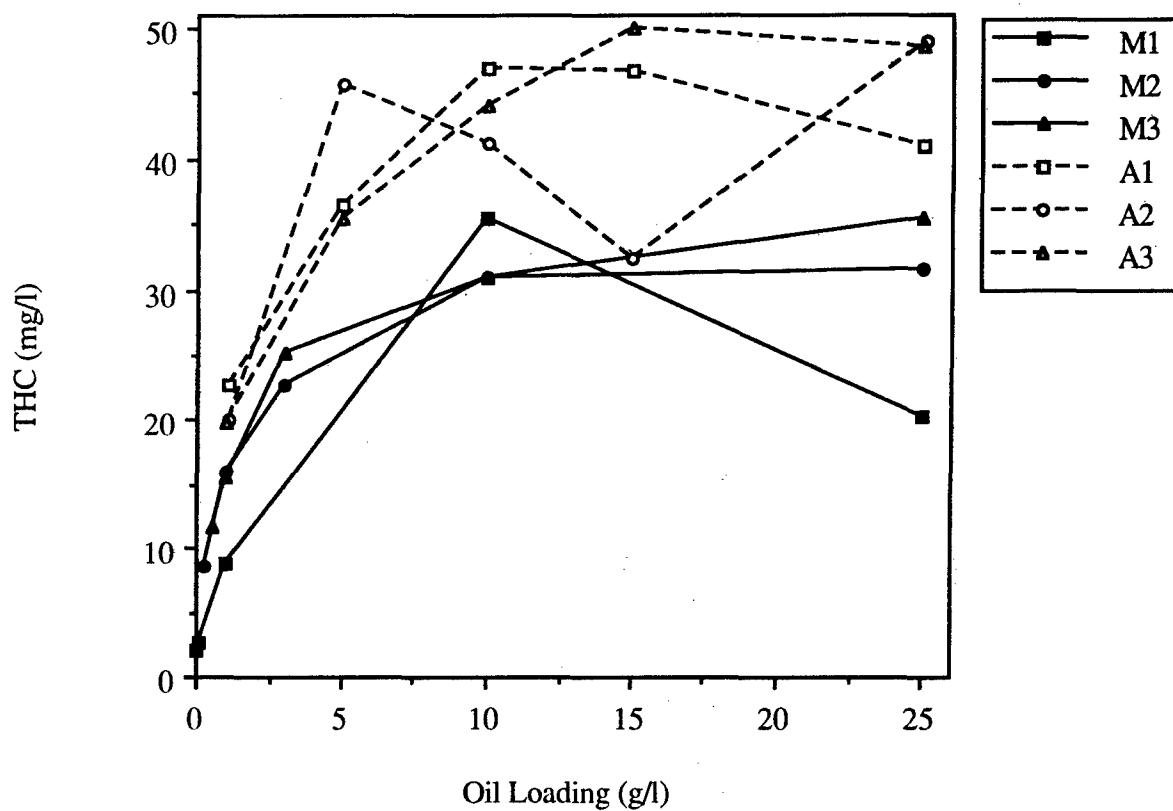


Figure 13. THC concentrations of initial WAF toxicity test solutions. M = mysid tests, A = abalone tests (all data points,  $n = 1$ ).

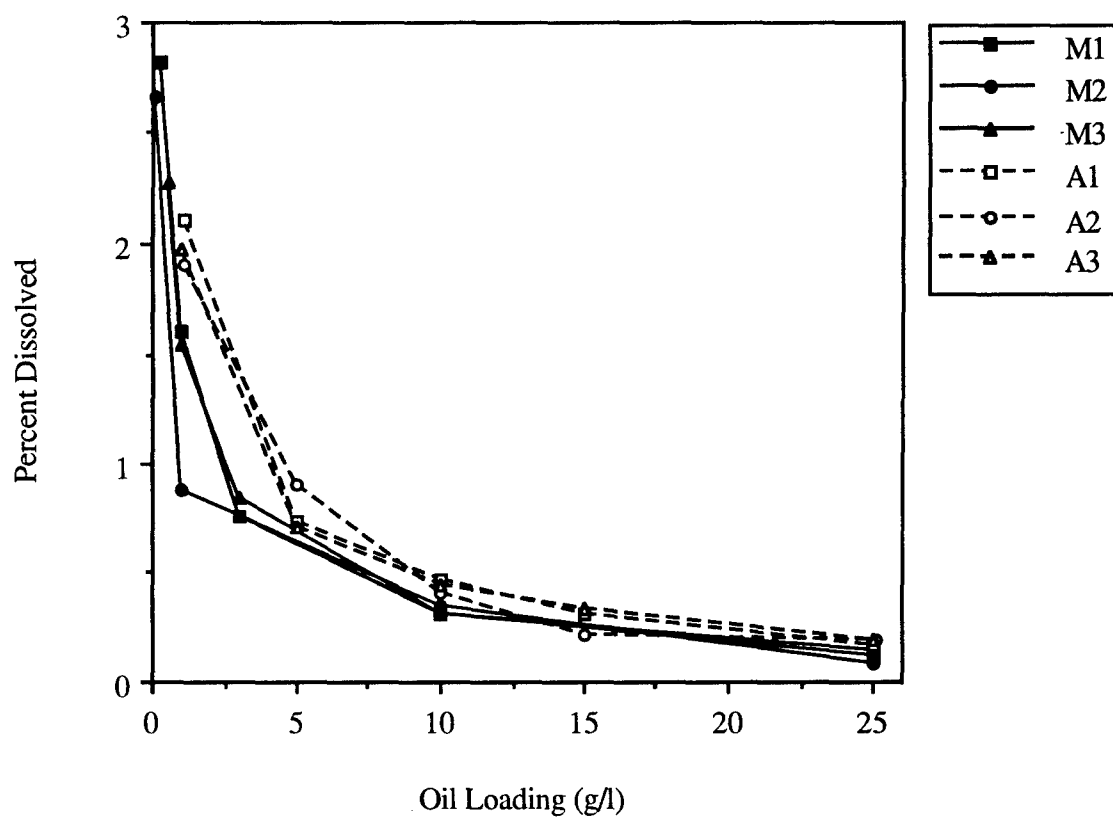


Figure 14. Percent of original oil dissolved (mg/L THC + mg/L loading) in initial WAF toxicity test solutions. M = mysid tests, A = abalone tests (n = 1).

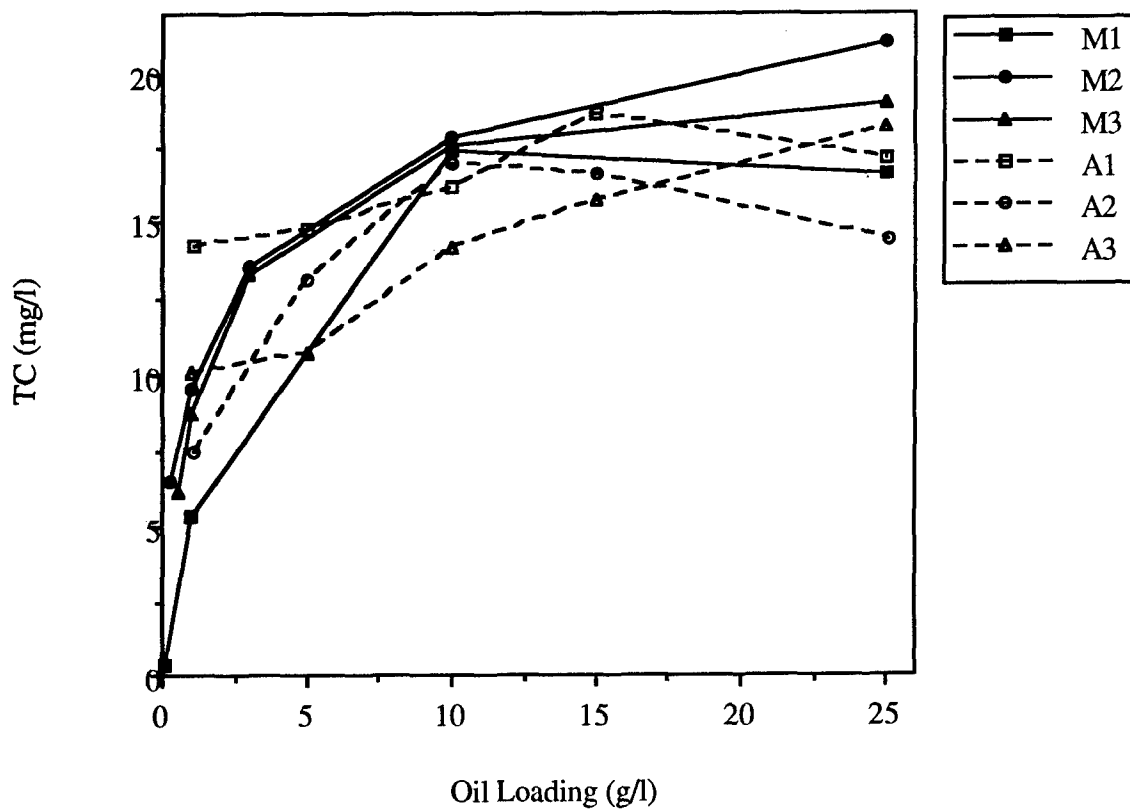


Figure 15. TC concentrations of initial WAF toxicity test solutions. M = mysid tests, A = abalone tests (all data points,  $n = 1$ ).

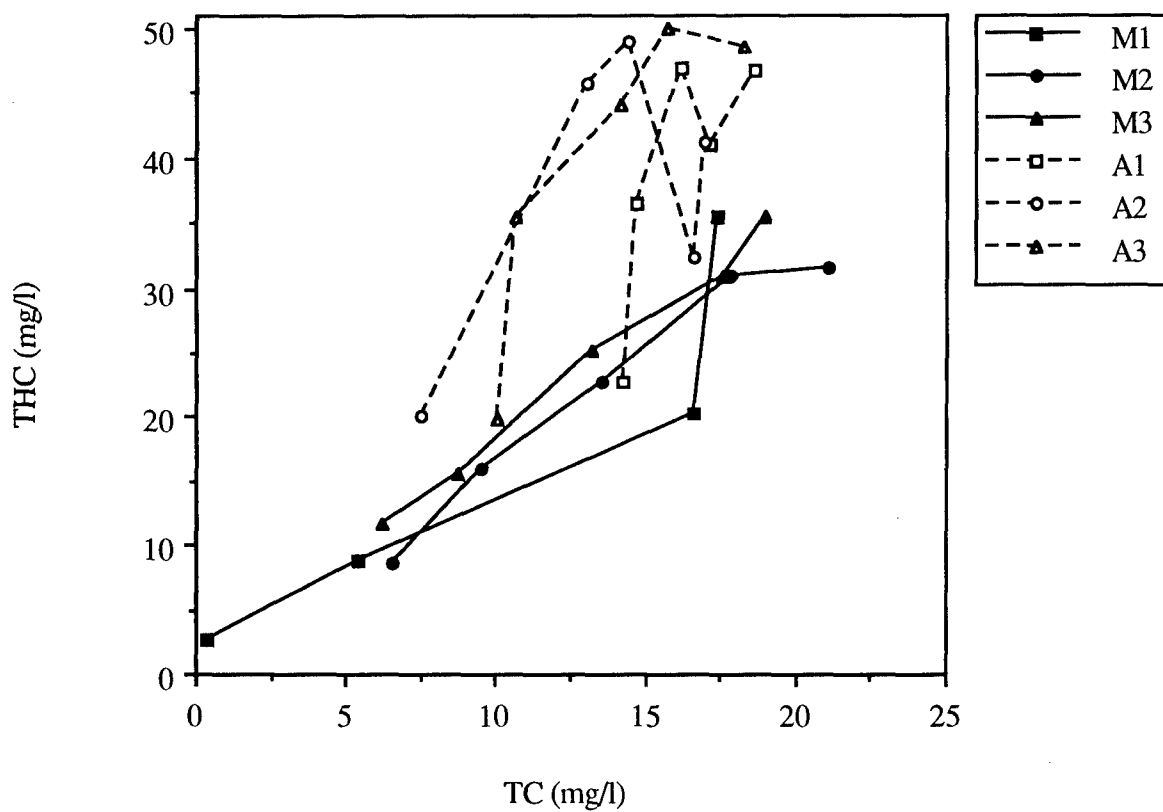


Figure 16. Relationship of THC versus TC in initial toxicity test solutions. M = mysid tests, A = abalone tests (n = 1).



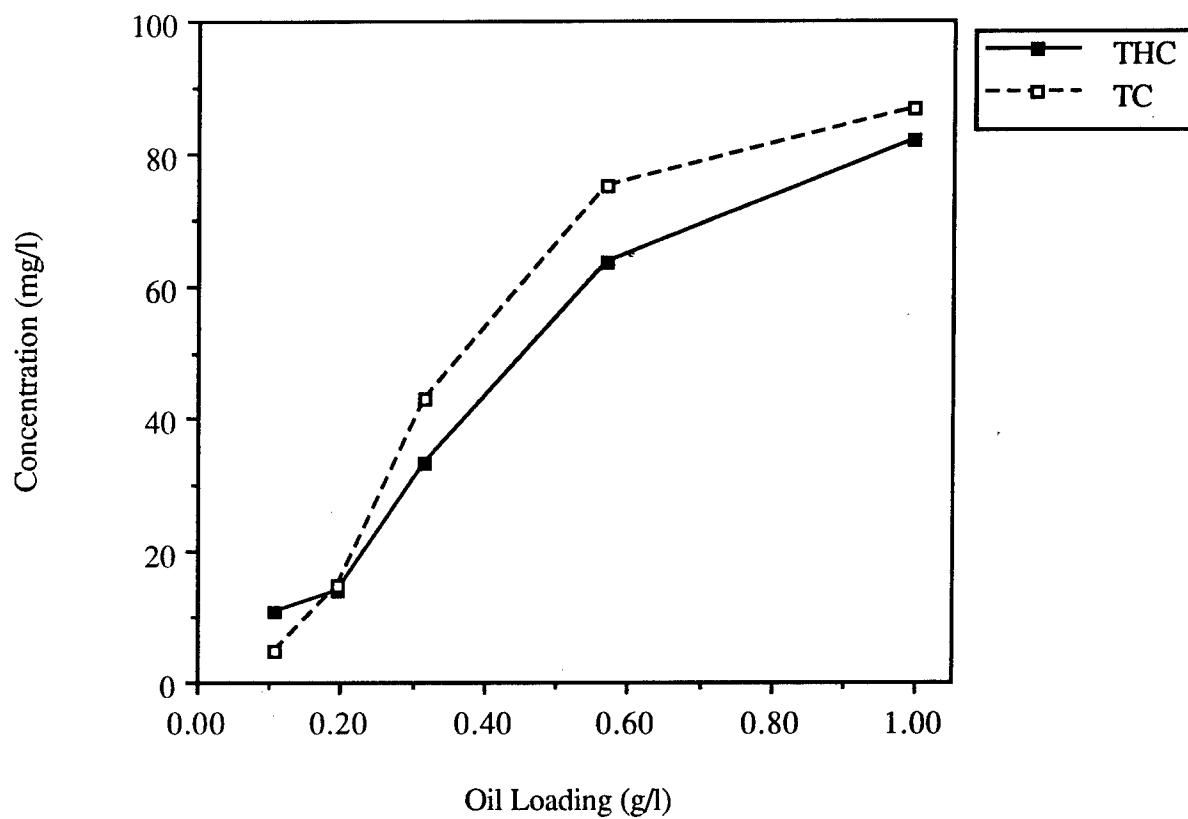


Figure 17. THC and TC concentrations at various oil loadings in initial mysid chemically dispersed oil toxicity test solutions (n = 1).

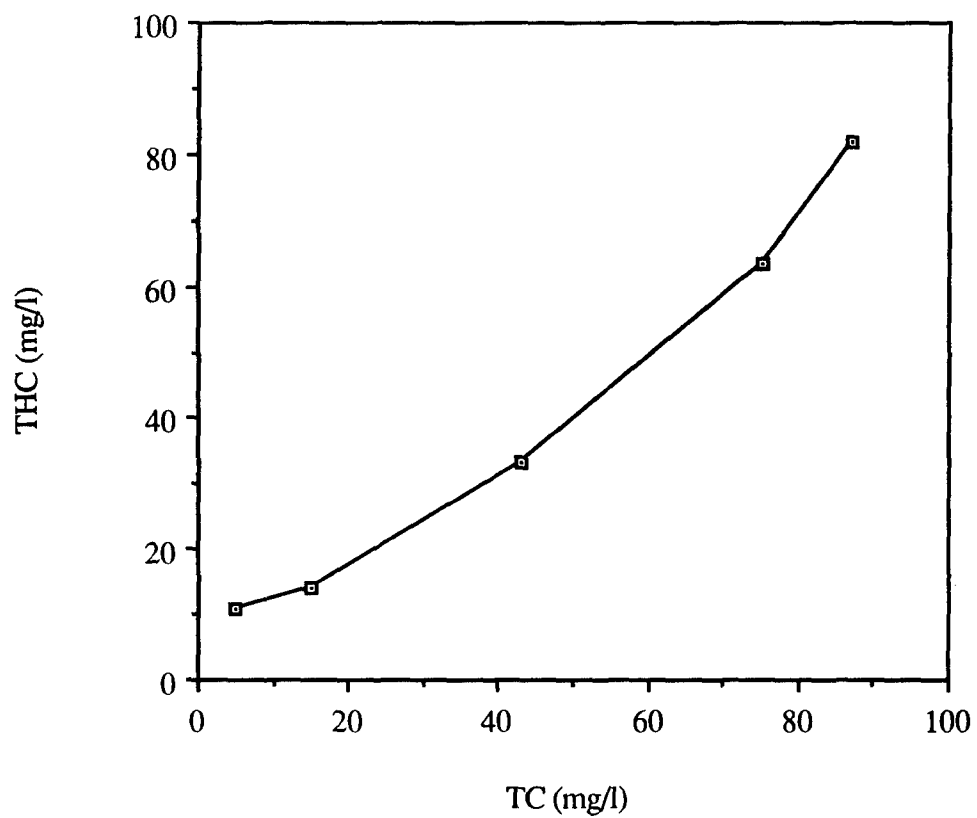


Figure 18. Relationship of THC to TC in initial mysid chemically dispersed oil toxicity test solutions (n = 1).

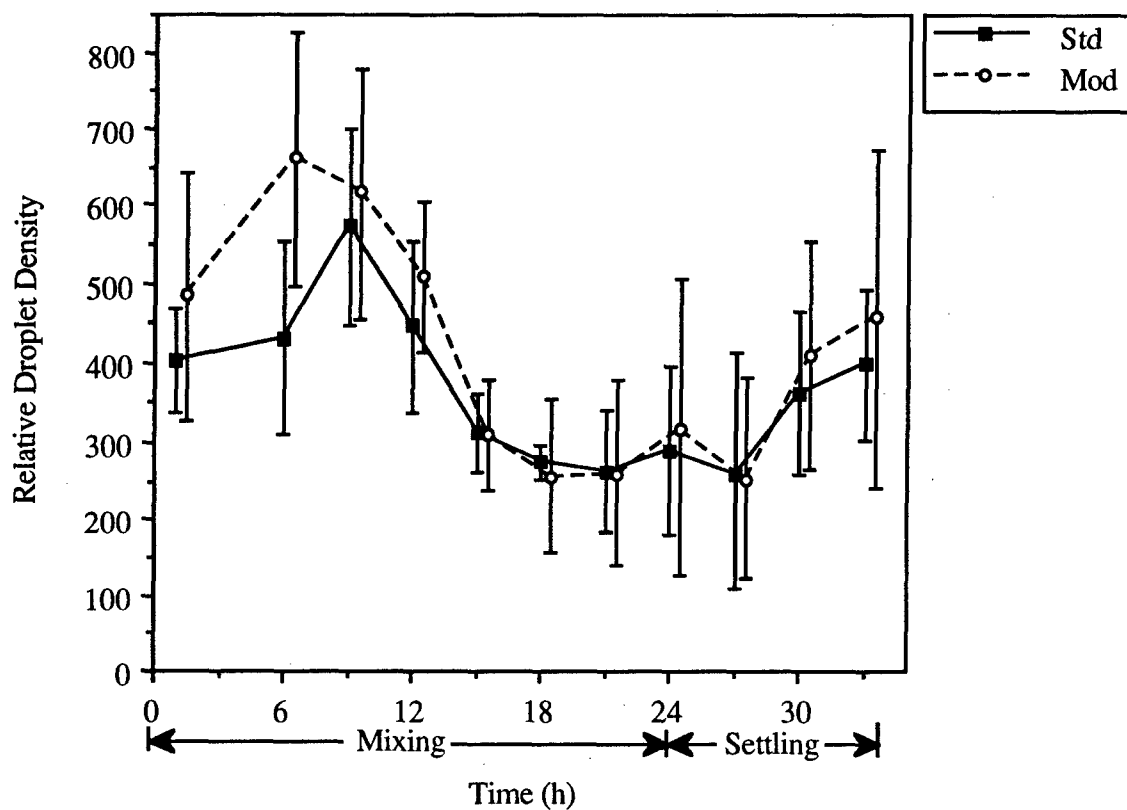


Figure 19. Relative droplet densities of 1 g/L oil loading dispersions using the two dispersion preparation methods. Data are mean  $\pm$  SD ( $n = 4$ ). Actual sampling times were equivalent; modified method data are offset for clarity.

## TOXICITY TESTING

### Test Materials

Alaskan North Slope (Prudhoe Bay) Crude was selected as the test oil for two main reasons: 1) it is heavily imported into California and therefore is both the most likely to be involved in a major spill, and of special interest to OSPR, and 2) it has been designated by the U.S. EPA as a reference oil and is available from their Reference Materials Repository, now administered by Resource Technology Corporation (Laramie, WY).

Corexit 9527 (Exxon Chemical Corp., Houston, TX) was selected as the dispersant used during this investigation because its toxicity has already been thoroughly evaluated in our laboratory using our current apparatus and techniques (Singer *et al.* 1990b, 1991), and because it is, at present, the most commonly stockpiled dispersant in the state of California. The overall research program will eventually test all other dispersants licensed in the state with several of the most frequently transported oils in order to provide comparative data for ranking in cooperation with state personnel.

### Test Organisms and Procedures

Testing will involve two species, the red abalone (*Haliotis rufescens*) and a kelp forest mysid (*Holmesimysis costata*). Both are considered key species based on previous data on the toxicity of a suite of four different marine species, and are recognized by the State for municipal discharger NPDES (National Pollution Discharge Elimination System) compliance testing. They are diverse trophically and taxonomically, and are both residents of nearshore waters along a significant portion of the California coast. *Haliotis* is of both ecological and economic importance in the state; its larvae are free-swimming and are spawned at several times during the year, and, as adults, supports a lucrative commercial industry. *Holmesimysis* is one of many crustacean species inhabiting nearshore kelp forests canopies, and while of little value economically, is an important food item for many kelp forest fish species that are recreationally and commercially exploited (Hobson and Chess 1976, Singer 1985). In past testing involving several dispersants under declining-exposure conditions, the *Haliotis* test was proved to be the most sensitive to all agents, and *Holmesimysis* represents the most ecologically relevant species in that it is present and reproductive in kelp forest canopies year round.

The specific toxicity test protocols for these two species were somewhat different. *Haliotis* tests involved the use of newly fertilized embryos, and used larval shell development as a sublethal endpoint. Gametes were obtained from spawning of in-house broodstock. Approximately 1000 embryos were introduced into test chambers prior to the first cell division. After 48 h, the time necessary to reach the free-swimming veliger stage (Leighton 1974), 100 haphazardly selected larvae were examined microscopically for abnormality of the larval shell. In past testing using surfactant-based dispersants, we have found that few, if any, "abnormal" larvae are ever found; the vast majority of embryos that do not develop into normal veligers were either arrested prior to blastula formation, or appeared to be groups of lysed and/or dissociated cells.

*Holmesimysis* tests involved 3-d-old juveniles, and measured lethality. Juveniles were obtained from wild-caught, gravid females collected from inshore kelp forests. The young go through larval development within the female's marsupium. Females with full marsupia were cultured in the laboratory until metamorphosed juveniles were released. Juveniles were cultured on *Artemia* nauplii both before and during toxicity testing. Eight juveniles were introduced into each test chamber.

Our exposure system has been specifically designed for testing microscopic marine organisms under closed, flow-through conditions (Singer *et al.* 1990a, 1991, 1993). The

system consists of sealed glass exposure chambers in a temperature-controlled bath (Figure 20). Filtered, aerated diluent is delivered directly to each exposure chamber by means of a multi-channel, unified-drive peristaltic pump. Effluent from each chamber can be directed either to waste or to a sampling tube for collection and analytical measurement. The chambers are essentially glass tubes with an integral fritted glass disk for test organism containment and an O-ring sealed flange held together by a full-circumference aluminum clamp, and is the approximate size of a standard 250 or 300 mL beaker (Figure 21). The chamber has two upper ports; one O-ring sealed for diluent inflow, and one with a teflon septum for introducing food through a syringe. Waste solution flows out the lower port where it can be collected with a syringe for concentration verification. All wetted components of the system are constructed of either borosilicate glass, teflon, or silicone to ensure chemical inertness.

In past sea trials at test spills, dispersant and/or oil concentrations at various depths below slicks have been seen to fall below detectable limits within several hours (Mackay and Wells 1983, Bocard *et al.* 1984). Traditional constant-concentration toxicity test methods would therefore be expected to overestimate to toxicity of both oil and dispersants, as compared to field use situations. Thus, spiked-exposure toxicity tests will be carried out. "Spiked" exposure, as opposed to pulsed or other episodic forms of toxicant exposure, refers to a dosing method wherein organisms are introduced into test chambers which are prefilled with toxicant solution followed by immediate initiation of dilution by direct flow of diluent through the chamber. Exposure chamber effluent is sampled hourly for 7 h after test initiation in order to define the concentration decline profile for each chamber. While it is impossible to simulate all possible field situations (or, indeed, any to a sufficient degree of "reality"), our spiked-exposure test procedures offer a blend of elementary field situation-based modeling and the necessary amount of laboratory rigor to achieve good quality control.

Each test consisted of six treatments; five toxicant concentrations and a seawater diluent control. Variation both within and among test populations was assessed by using three replicate exposure chambers within each test treatment and by running three replicate tests for each species-toxicant combination. No-effect and median-effect concentrations were estimated using established statistical methods (Zar 1974, Hamilton *et al.* 1977). Reproducibility of toxicity data was assessed using the coefficient of variation (C.V.) of median-effect estimates for the triplicate tests (Schimmel *et al.* 1989).

Triplicate WAF toxicity tests were completed with both the red abalone (*Haliotis rufescens*) and mysid (*Holmesimysis costata*). Because of strict criteria surrounding the rates at which toxicants are flushed from our test system in order for all tests to be statistically comparable, a larger number of tests were performed, however, only those meeting rate acceptability criteria are reported here. Also, a single, preliminary chemically dispersed oil test with mysids was completed.

WAF stocks were prepared according to the procedures specified in Appendix 1. Upon completion of mixing, approximately 1–1.25 L of each WAF was drained from the aspirator bottle by means of a silicone tube directly into a fully evacuated Tedlar® gas-sampling bag (Aerovironment, Monrovia, CA), eliminating any atmospheric exposure (Singer *et al.* 1990a,b). Exposure chambers were filled directly from the bags by means of a silicone tube, and were then sealed until the introduction of test animals. Animals were added to the chambers in random order at the appropriate density (8 *Holmesimysis* juveniles, ≈1,000 *Haliotis* embryos) by unsealing the chamber, introducing the animals by pipette, and resealing the chamber; tests were then initiated by immediate commencement of flushing of all chambers with clean, aerated seawater at a rate of approx. 2 mL/min.

After 48 h, *Haliotis* larvae were removed from the exposure chambers and fixed in 5% buffered formalin and microscopically evaluated for morphological abnormalities (Hunt and Anderson 1989, Anderson *et al.* 1990). Two separate endpoints were assessed during *Holmesimysis* tests. The first was the standard mortality endpoint, in which mortality was visually assessed daily for 96 h, coincident with measurement of pH, DO concentration, and

temperature (Anderson *et al.* 1990). The second was a new, sublethal narcosis endpoint. In initial mysid tests, we observed that in higher concentration treatments, most or all animals appeared to be dead almost immediately after being introduced into test chambers. However, during the course of conducting chemical sampling in the initial hours of exposure, these same animals were seen to return to swimming normally. We hypothesized that these observations were the result of initial narcosis from dissolved compounds which were either physically or chemically interrupting respiratory activity, or were being depurated at rates high enough to not cause permanent damage. Therefore, behavioral observations were made during the first 6–7 h of exposure coincident with chemical sampling for concentration decline profile verification. Observations consisted of tallying the number of animals active and inactive. Inactive animals were defined as those lying on the bottom of the test chamber (often upside-down), that were not roused by, or able to maintain normal upright orientation during, tipping and/or gently swirling the chamber.

### Abalone Toxicity Tests

*Haliotis* WAF tests were conducted at oil loading rates of 1 to 25 g/L. Loadings above 25 g/L were deemed useless, both because higher oil/water ratios were deemed fairly unrealistic, and because chemical data suggested that further loadings would not result in significantly more concentrated solutions. These loadings resulted in initial THC concentrations ranging from about 20 to 50 ppm.

Toxicity results showed no significant acute effect in any test treatments (Fig. 22, Table 5). At THC concentrations as high as 48.9 ppm, only about 12% mean effect was seen in these tests, which was not statistically different than the control treatments.

### Mysid Toxicity Tests

*Holmesimysis* WAF tests were conducted at similar loadings to *Haliotis* tests, with the exception that they ranged lower to better define patterns of narcosis; test loadings generally ranged from 0.01 to 25 g/L. The chemically dispersed oil (CDO) test was conducted at oil loadings of 0.1 to 1 g/L with a 10:1 oil:dispersant ratio.

Similar to abalone WAF test results, no significant mortality was seen in mysid WAF tests, with the single exception of the highest loading rate in test 2, which produced a mean mortality of 20.8 %, and which was significantly different from control treatment response (Fig. 23, Table 6). In the CDO test, though, statistically significant mortality was seen at two- to three-fold lower THC concentrations (corresponding to >100-fold less oil loading). Similarly, median lethal effect was seen in the CDO test at approximately one half, or less, the THC concentration as in WAF tests. These comparisons are considered preliminary until final procedures have been established for preparing CDO solutions and conducting toxicity tests, but even so, they do suggest a significantly higher effect in chemically mediated dispersions. Whether this difference is the result of physical effects of particulate oil, increased dissolved material as a result of dispersion, surfactant-mediated increased uptake of hydrocarbons, or some combination of these, remains to be seen in future research.

Data obtained from these tests on the narcotic effects of these solutions proved to be substantially more sensitive than mortality. Initial narcosis rates ( $\approx 15$  min after test initiation) were seen to be variable, based on THC concentration (Fig. 24). In the first test, significant effect was seen at <10 ppm, with concentrations >19 ppm producing 100% initial effect. However in the second and third tests, no effect was seen in concentrations up to about 16 ppm, with complete effect occurring above about 28 ppm. These patterns of somewhat variable sensitivity were also seen in subsequent data taken throughout the initial concentration decline phase of each test (Fig. 25). In general, loadings >1 g/L produced significant narcotic effects, from which full recovery was not seen for 5–7 h. It should be noted that recovery from initial narcosis occurred at the same time that toxicant

concentrations were declining as a result of introduction of clean seawater. At this time we do not have sufficient data to describe the relationship between concentration decline rate and narcosis recovery rate.

Significant narcotic effect in the CDO test was seen at a much lower loading (0.194 g/L), however, this loading yielded a THC concentration of 14.1 ppm, which was very similar to the effective concentrations in the WAF tests (Fig. 26); it must be noted here, though, that THC concentrations of WAFs were based only on the 10 or so compounds present, whereas those of CDOs were based both on soluble compounds, and on the hundreds of insoluble compounds associated with particulate oil. CDO test data also showed that at higher concentrations (30–85 ppm THC), recovery from narcotic effects was substantially slower, and incomplete. Also, slower recovery from narcosis was positively correlated with earlier mortality; this pattern remains to be validated by further testing.

### Summary of Toxicity Results

The most obvious conclusion that might be drawn from these data is that the soluble fractions of Prudhoe Bay crude oil exhibit low acute toxicity, even at unrealistically high oil/water ratios (1:40). By virtue of the method by which they are generated, these data are akin to “worst case scenario” conditions, in that the solutions used are saturated, and therefore represent a conservative estimate of concentrations foreseeable in the field. The conservative nature of these test treatments is further borne out by the fact that chemically they are dominated by the volatile BTEX compounds, which might be expected to escape rapidly in the field.

However, mysid narcosis data suggest that loadings as low as 1 g/L (1:1000 O/W) may result in effects which could have significant ramifications in field populations. Even though little or no outright mortality was seen in WAFs at concentrations as high as 40–50 ppm THC, effects that might produce population-level effects were seen at concentrations <10 ppm. Narcosis data may be of significant value in that while they are reversible in a laboratory situation, they can justifiably be considered an indicator of “ecological death” in the field (i.e. an animal that is incapable of avoidance of predators or escape to shelter is not likely to survive in the wild long enough to recover).

Data from the preliminary test with chemically dispersed oil showed that whereas acute effects were observed at significantly lower loadings, effective THC concentrations, while based on different sets of analytes, were similar between CDO and WAF tests. These data cannot, however, address the question as to the mechanism to which the differences in effective loadings might be attributed; physical effects of particulate oil, chemical effects from increased dissolved fraction concentrations, or effects attributed to the dispersant (either direct dispersant toxicity, or surfactant-mediated enhancement of uptake). Past data collected on the toxicity of Corexit 9527 alone suggest that direct dispersant toxicity cannot be ruled out as playing a role in CDO test results. NOECs in dispersant-only toxicity tests with Corexit 9527 determined in our laboratory ranged from 8.4–20.5 ppm (Singer *et al.* 1991). The estimated LC50 of CDO was 0.21 g/L loading, which corresponds to a dispersant loading of approximately 20 ppm (10:1 O:D ratio). Therefore, it is conceivable that even though <100% dissolution of the dispersant into the test solution is assumed, effects of the dispersant cannot be ruled out as perhaps contributing to the results seen. Given that theoretical dispersant concentrations are at least in the range of toxicity results seen in previous testing, it is plausible that some level of effect may be present, and thus may be acting additively or synergistically on test animals.

Table 5. Results of Prudhoe Bay crude oil WAF toxicity tests using *Haliotis* embryos.

Test #	NOEC		EC50	
	g/L Oil Loading	ppm THC	g/L Oil Loading	ppm THC
1	>25.00	>41.03	>25.00	>41.03
2	>25.07	>48.92	>25.07	>48.92
3	>24.99	>48.56	>24.99	>48.56

Table 6. Mortality results from Prudhoe Bay crude WAF and chemically dispersed oil on juvenile *Holmesimysis*.

Test #	NOEC		EC50	
	g/L Oil Loading	ppm THC	g/L Oil Loading	ppm THC
WAF 1	>25.00	>20.23	>25.00	>20.23
2	10.00	30.99	>25.00	>31.54
3	>24.99	>35.48	>24.99	>35.48
CDO 1	0.108	10.71	0.21 (0.18, 0.24) <sup>1</sup>	18.15 (15.64, 21.06) <sup>1</sup>

<sup>1</sup> 95% confidence limits.



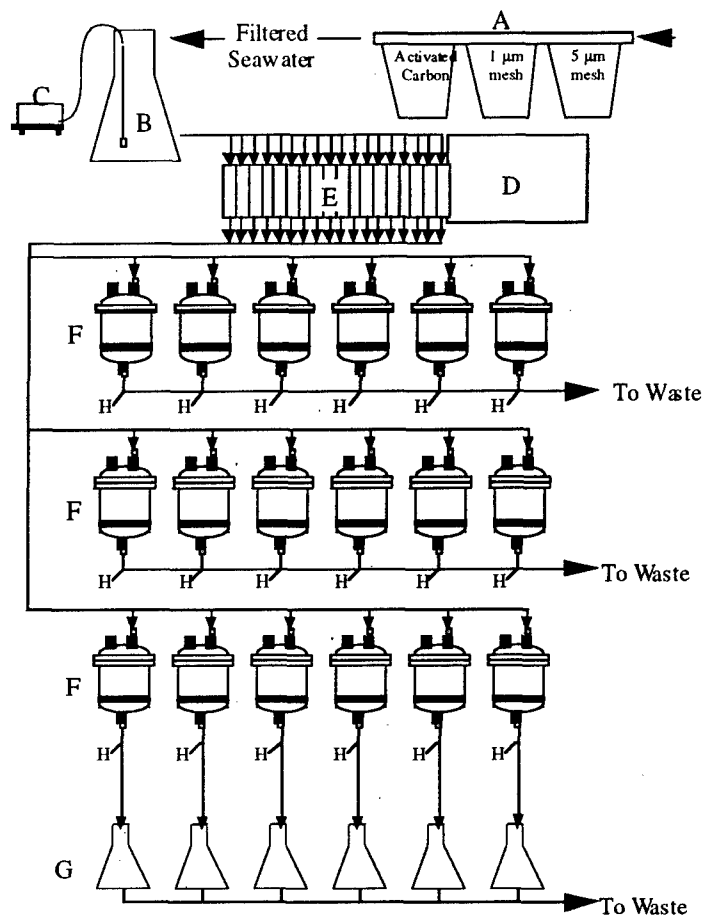


Figure 20. Schematic diagram of the exposure system showing flow patterns and main system components. A, cartridge filters; B, seawater head tank; C, aeration pump; D, peristaltic delivery pump; E, cartridge pump heads (18); F, exposure chambers; G, water quality sampling flasks; H, chemistry sampling ports.

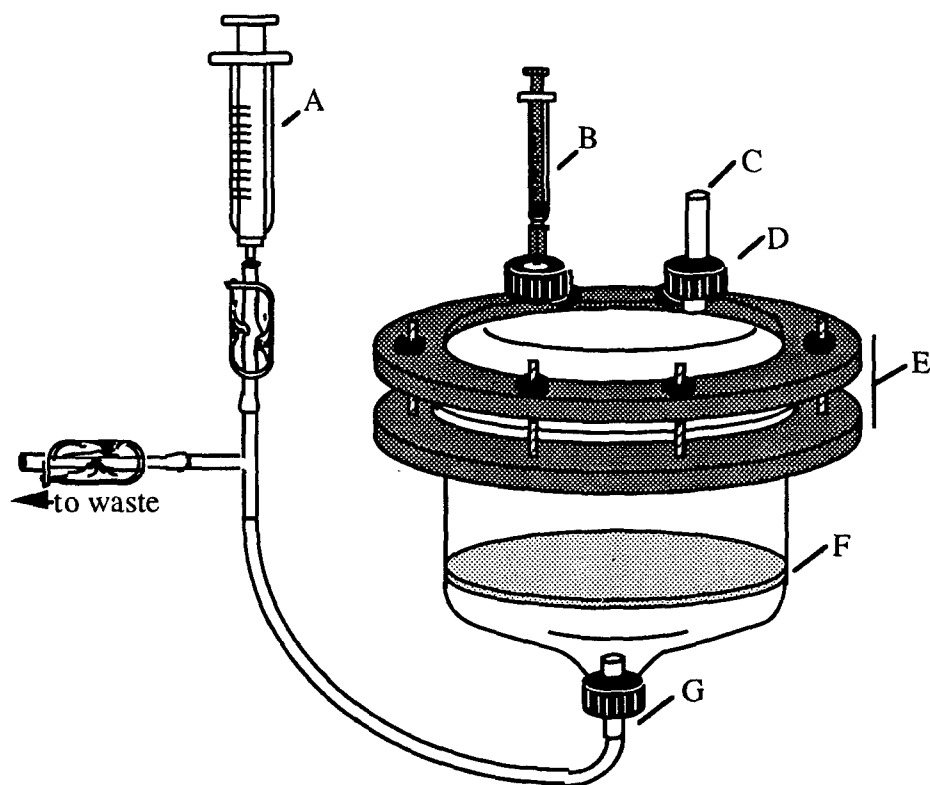


Figure 21. Schematic diagram of the toxicity test exposure chamber: A. Glass syringe for chemistry sampling; B, syringe for food introduction; C, Diluent inlet; D, threaded glass fittings with phenolic caps; E, silicone O-ring sealed glass flange with clamp; F, fritted glass disk; G, discharge outlet.

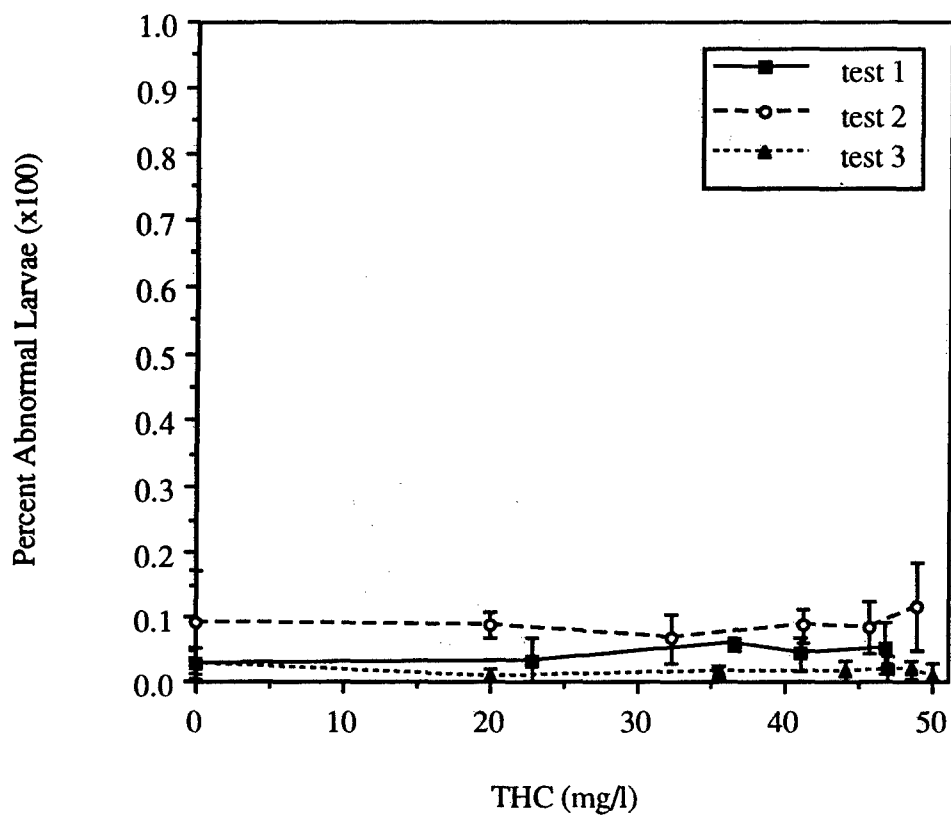


Figure 22. Dose-response relationships for abalone Prudhoe Bay crude oil WAF toxicity tests. Data points represent mean  $\pm$  SD ( $n = 3$ ).

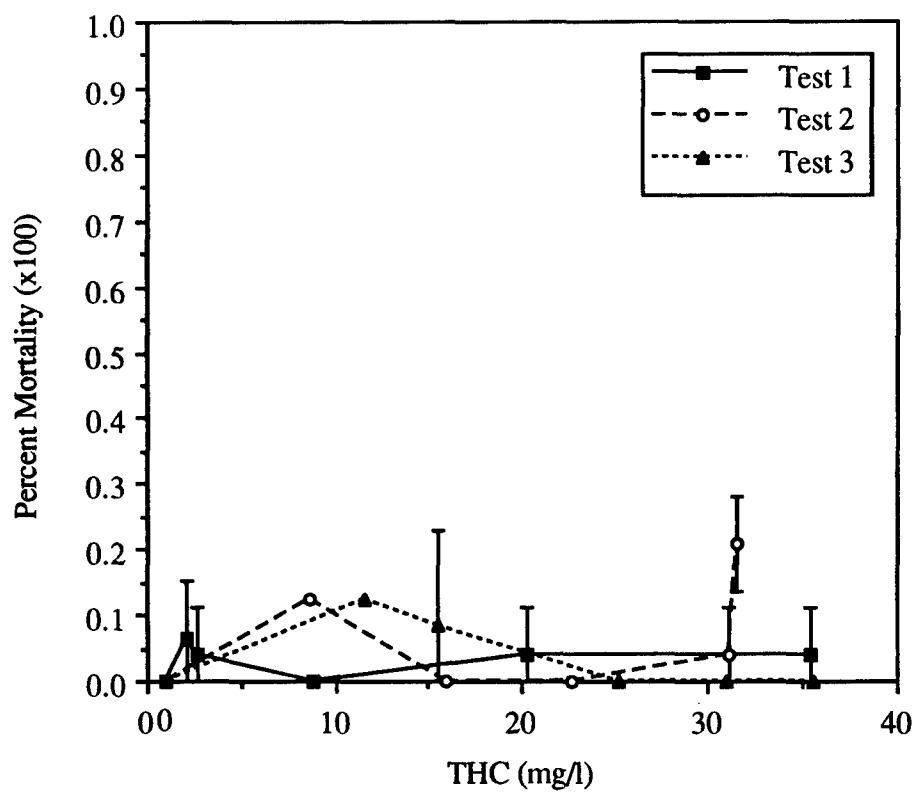


Figure 23. Dose-response relationships for mysid Prudhoe Bay crude oil WAF toxicity tests. Data points represent mean  $\pm$  SD (n = 3).

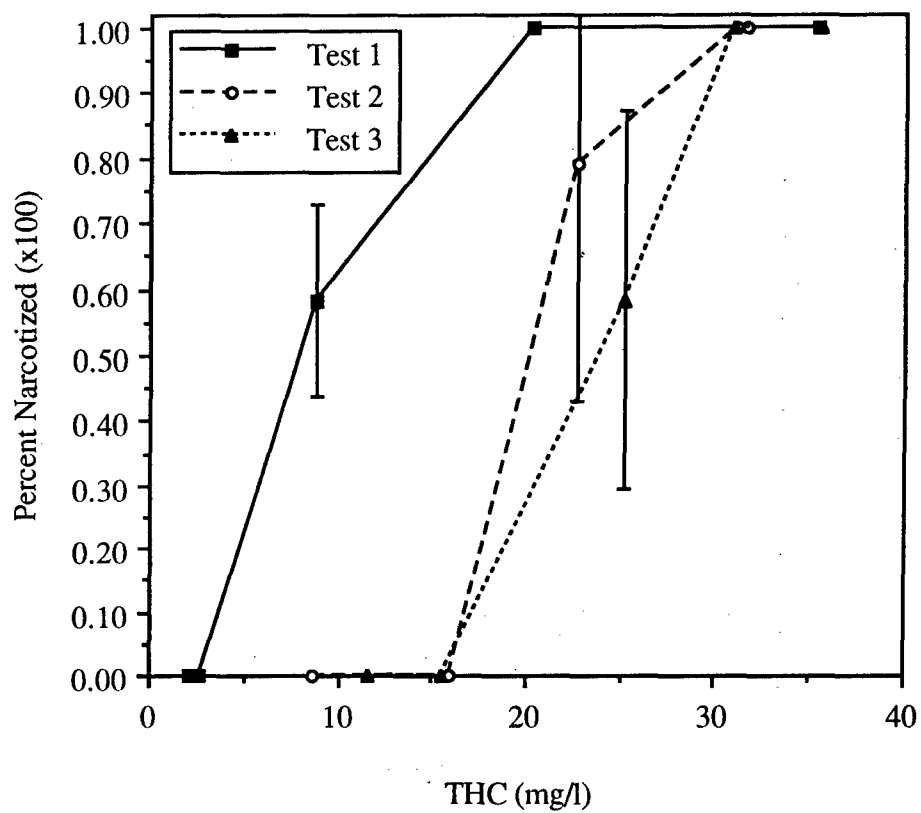


Figure 24. Initial narcosis dose-response relationships for mysid WAF toxicity tests. Data points represent mean  $\pm$  SD (n = 3).

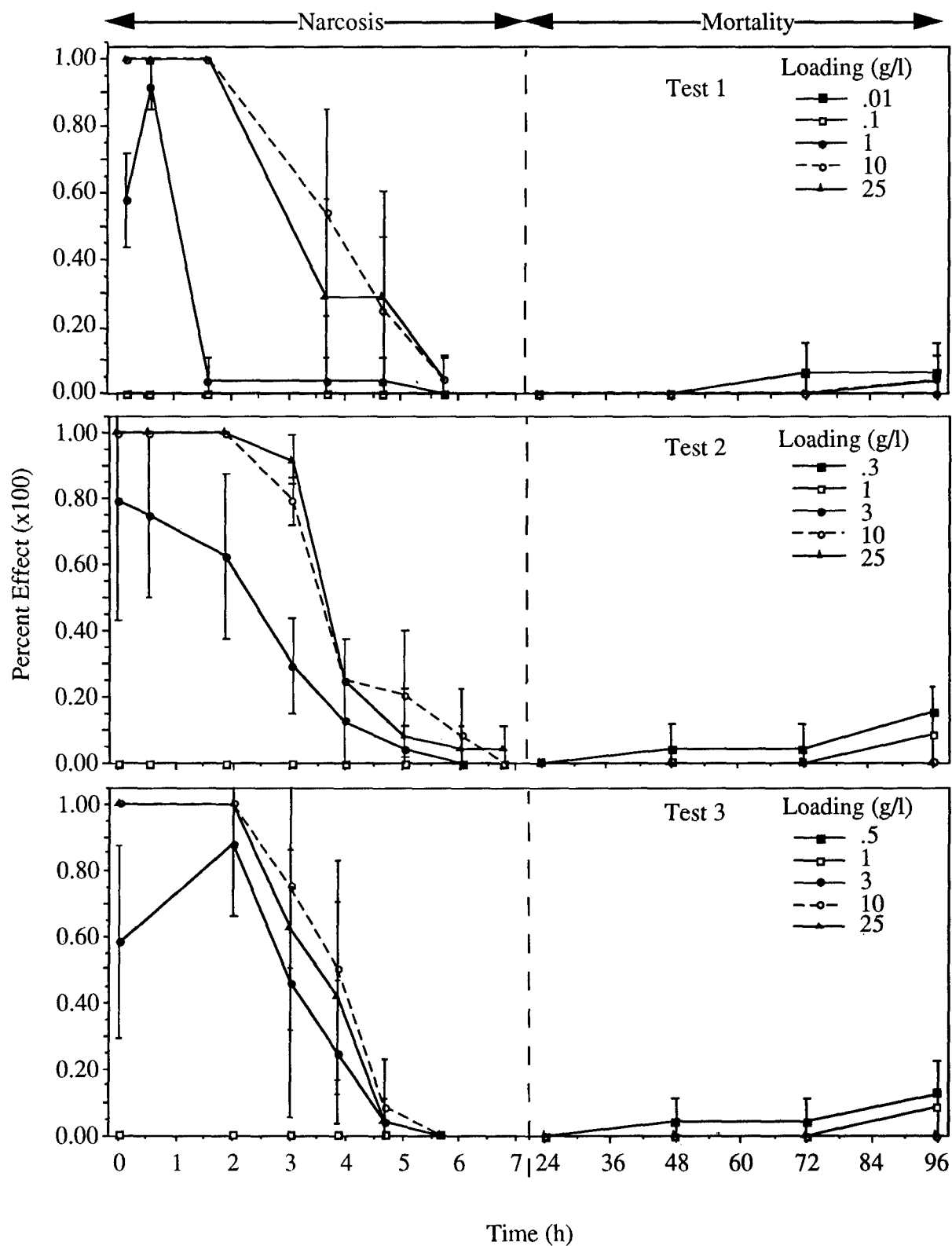


Figure 25. Narcosis rate versus time for replicate mysid WAF tests. Data points represent mean  $\pm$  SD ( $n = 3$ ).

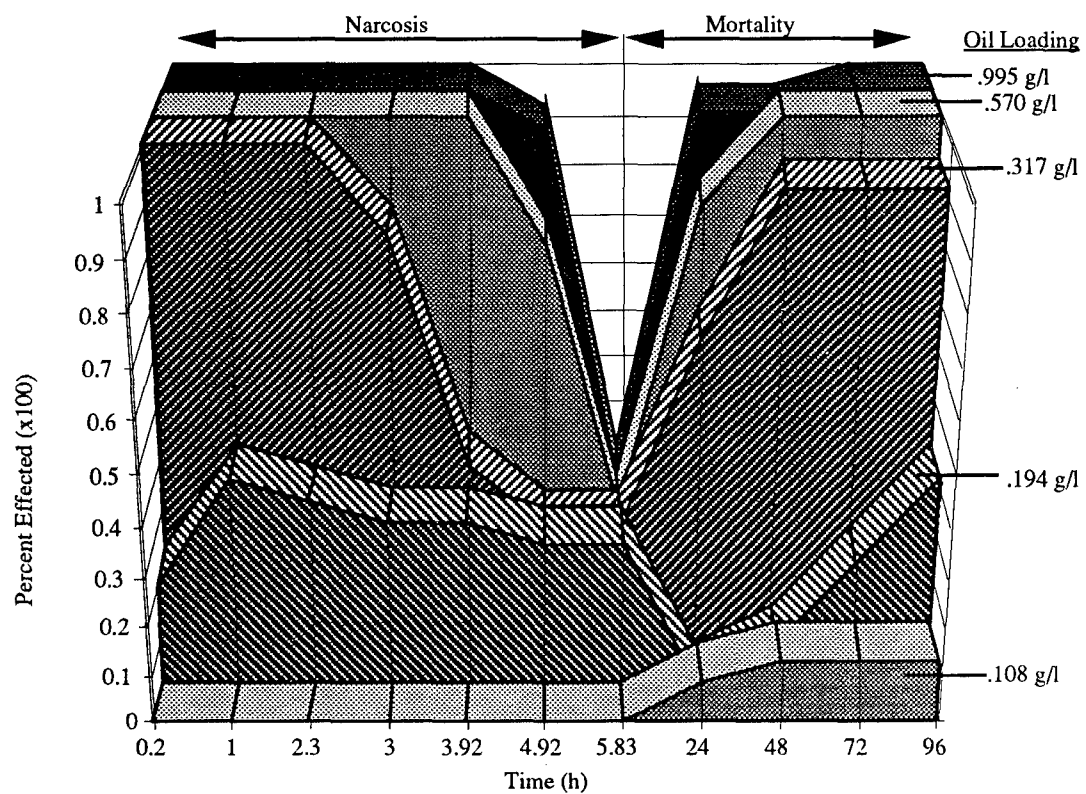


Figure 26. Mean narcosis and mortality (n = 3) for mysid chemically dispersed oil test.

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## Appendix 1

### Draft Protocol for Preparation of a Water-Accommodated Fraction of Crude Oil

**Subject: Preparation of Water Accommodated Fraction of Crude Oil or Petroleum Products for Toxicity Testing**

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**D R A F T**

**Equipment needed:**

1. Aspirator bottles of appropriate size, one for each test treatment (sidearms fitted with silicone tubing and clamp).
2. Stoppers for above: either rubber stoppers wrapped with teflon tape or teflon coated stoppers.
3. Teflon coated magnetic stir bars (e.g. 25 mm long x 10 mm diam. for 2 L bottles); one for each bottle.
4. Variable speed stir plates, one for each bottle, with capability of verifying constancy of rotation speed, either by use of an external tachometer, or by internal digital readout (electromagnetic type preferred).
5. Analytical balance; 4 kg minimum recommended for direct oil weighing, 0.001 g accuracy required if indirect weighing by syringe.
6. Temperature control bath, chamber, or room.
7. Graduated cylinder(s) (optional).
8. Aluminum foil (optional).
9. Gas-tight syringe(s) (optional).

**Procedure:**

- 1.0 Determine a volume of water which reaches just to the top of the straight part of the aspirator bottle sides (e.g.  $\approx$  1860 mL for a 2L bottle).
- 2.0 Filter enough seawater for all treatments, including controls, by passing water through a nominal 0.45  $\mu$ m pore filter. Then equilibrate both water and test material to required test temperature.
- 3.0 Add required amount of water to aspirator bottle.
  - 3.1 Preferred method is by weight, if feasible. First tare scale with bottle, stir bar, tubing, and clamp, then weigh water directly into bottle to nearest 0.01 g.
  - 3.2 Alternatively, for large volumes, add water by volume to nearest 1.0 mL.
- 4.0 Add required amount of test material directly onto water.

**Subject: Preparation of Water Accommodated Fraction of Crude Oil or Petroleum Products for Toxicity Testing**

---

**D R A F T**

- 4.1 For small volume containers and large loading rates, preferred method is to deliver test material directly onto water with bottle on scale (tared after water addition).
- 4.2 Alternatively, deliver test material via gas-tight syringe, recording syringe weight before and after material delivery to nearest 0.001 g. Calculate actual weight of material delivered by subtraction.
- 5.0 Seal bottle immediately and place on stir plate in either constant temperature room or water bath. Great care should be taken to avoid stranding oil on bottle walls when moving to stir plate.
- 6.0 Begin stirring and adjust stirrer speed to  $200 \pm 10$  rpm. Ensure that no vortex is formed at this speed; if so, either reduce speed until no vortex is present or (preferably) restart preparation with smaller stir bar. Speed should be monitored frequently for the first few hours, and readjusted as needed.
- 7.0 When all bottles are started, preparation should proceed in darkness either by wrapping bottles in aluminum foil, or placing stirrers in a light-tight chamber or room.
- 8.0 Stir for a minimum of 24 h, and use solutions as soon as possible thereafter. Solutions are usable after 24 h and before 48 h of stirring.
  - 8.1 No settling time is required after stirrers are stopped.
- 9.0 Drain solution from aspirator bottle making sure not to get any of the surface slick in the receiving vessel. Waste the first few milliliters to clear sidearm and tubing then rinse transfer vessel, if used. Aspirator bottles should be drained either directly into test vessels or into collapsible (zero-headspace) transfer vessels, i.e. teflon gas-sampling bags, or equivalent.
  - 9.1 Fill test vessels with solution and seal as quickly as possible to avoid volatilization.

## Appendix 2

### Draft Protocol for Preparation of Chemically Dispersed Crude Oil

**Subject: Preparation of Chemically-Mediated Dispersions of Crude Oil or  
Petroleum Products for Toxicity Testing**

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**D R A F T**

**Equipment needed:**

1. Aspirator bottles of appropriate size, one for each test treatment (sidearms fitted with silicone tubing and clamp).
2. Stoppers for above: either rubber stoppers wrapped with teflon tape or teflon coated stoppers.
3. Teflon coated magnetic stir bars (e.g. 25 mm long x 10 mm diam. for 2 L bottles); one for each bottle.
4. Variable speed stir plates, one for each bottle, with capability of verifying constancy of rotation speed, either by use of an external tachometer, or by internal digital readout (electromagnetic type preferred).
5. Analytical balances; 4 kg minimum recommended for direct water weighing, 0.001 g accuracy required for test material weighing by syringe.
6. Temperature control bath, chamber, or room.
7. Graduated cylinder(s) (optional).
8. Aluminum foil (optional).
9. Gas-tight syringes.

**Procedure:**

- 1.0 Determine a volume of water which reaches just to the top of the straight part of the aspirator bottle sides (e.g.  $\approx$  1860 ml for a 2L bottle).
- 2.0 Filter enough seawater for all treatments, including controls, by passing water through a nominal 0.45  $\mu$ m pore filter. Then equilibrate both water and test materials to required test temperature.
- 3.0 Add required amount of water to aspirator bottle.
  - 3.1 Prerinse clean bottle with test seawater and drain.
  - 3.2 Preferred method is by weight, if feasible. First tare scale with bottle, stir bar, tubing, and clamp, then weigh water directly into bottle to nearest 0.01 g.
  - 3.3 Alternatively, for large volumes, add water by volume to nearest 1.0 ml.

**Subject: Preparation of Chemically-Mediated Dispersions of Crude Oil or Petroleum Products for Toxicity Testing**

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**D R A F T**

- 3.4 Tilt bottle sufficiently to remove all air bubbles from sidearm, then place bottle on stir plate.
- 4.0 Begin stirring water, set stirrer speed to achieve 20–25% vortex.
  - 4.1 To set vortex depth, measure height of water volume, then measure down 25% of height from water surface and apply registration mark onto bottle. Set stirrer speed so that steady vortex does not penetrate water column below mark.
- 5.0 Add required amount of test materials directly onto water.
  - 5.1 Calculate required volume of test materials (both oil and dispersant) needed based on density (e.g. 100 mg oil needed ÷ 0.89 g/mL = 112 µL needed). Volume of dispersant needed can be calculated by dividing oil amount by dispersant/oil ratio (e.g. 10:1 oil:dispersant ratio = 112 µL oil ÷ 10 = 11.2 µL dispersant).
  - 5.2 Draw oil and dispersant into separate appropriately sized gas-tight syringes. Weigh syringes before (filled) and after delivery, and calculate actual mass of each delivered by difference.
  - 5.3 Deliver oil first into center of stable vortex; deliver fast enough to maintain a constant stream, but not so fast as to force oil below water surface. Syringe needle tip should not contact water surface. Then immediately deliver dispersant into vortex/oil mass center. Stirrer speed should be monitored frequently for the first few hours, and readjusted as needed.
- 6.0 Seal bottle immediately.
- 7.0 When all bottles are loaded, stirring and settling should proceed in darkness either by wrapping bottles in aluminum foil, or maintaining stirrers in a light-tight chamber or room.
- 8.0 Stir for a minimum of 18–24 h, discontinue stirring, and let solutions settle 6 h. Use solutions as soon as possible thereafter.
- 9.0 Drain solution from aspirator bottle making sure not to get any of the surface slick in the receiving vessel. Waste the first few milliliters to clear sidearm and tubing then rinse transfer vessel, if used. Aspirator bottles should be drained either directly into test vessels or into collapsible (zero-headspace) transfer vessels, i.e. teflon gas-sampling bags, or equivalent.
  - 9.1 Fill test vessels with solution and seal as quickly as possible to avoid volatilization.



**INFLUENCE OF DISPERSANTS ON PETROLEUM BIOAVAILABILITY WITHIN A  
MARINE FOOD CHAIN**

*Martha F. Wolfe, Ronald Tjeerdema, University of California*

## EXECUTIVE SUMMARY

Crude oil released in the marine environment poses a serious threat to sensitive shorelines and organisms that live and interact at the surface of the water. In an effort to reduce the risk of loss to these marine populations and coastlines, chemical dispersing agents may be employed to increase the solubility of many of the constituents of the crude oil and break up a slick. In the process, increased concentrations of these constituents may move into the water column, enhancing their bioavailability to the marine organisms present. In addition, chemical dispersing agents may alter the uptake of petroleum hydrocarbons through alterations in osmoregulation, membrane permeability, or other mechanisms at a cellular level. Because organisms such as phytoplankton play a role in the fate of dispersed oil, it is important to understand how dispersants may influence the bioavailability of petroleum hydrocarbons in primary trophic levels of marine food chains.

In order to examine changes in bioavailability, an appropriate exposure media was selected for both the water accommodated fraction (WAF) of Prudhoe Bay crude oil (PBCO) and a dispersed oil (DO) mixture of PBCO and Corexit 9527®, and methods were developed to prepare and characterize an exposure media with consistent composition. Culturing techniques were learned and a large scale facility was set up to culture *Isochrysis galbana* for exposure studies. Glassware was obtained and customized for exposure chambers for temperature controlled, closed system, exposures. Methods were developed to collect compounds and metabolites and isolate them from exposure media samples. Finally, analysis techniques were designed for the separation, identification, and quantitation of products.

The overall experimental design evaluated bioavailability of petroleum hydrocarbons in terms of uptake, bioaccumulation, and metabolic fate using a customized temperature controlled, closed system, exposure chambers. The golden brown algae, *Isochrysis galbana*, a primary producer, was used to determine the influence of the model dispersing agent, Corexit 9527. Organisms were exposed to laboratory preparations of WAF and DO spiked with <sup>14</sup>C-naphthalene, a model hydrocarbon, at concentrations below the determined NOEL. Samples were collected over a series of time points during the exposure period. Uptake was determined by the amount of algae associated <sup>14</sup>C. Solid phase extraction (SPE) techniques were used for the collection and concentration of parent compound and metabolites from exposure media. A simple digestion was used to prepare algae material for analysis. High pressure liquid chromatography (HPLC) co-chromatography was used to fractionate and identify metabolic products. Quantitation was done with liquid scintillation counting.

Results of the studies indicate that the presence of the dispersing agent, Corexit 9527®, has minimal influence (<10%) on the uptake of naphthalene from PBCO by *Isochrysis galbana*. The

increase in observed uptake is comparable to the increased concentration of naphthalene in the presence of dispersant. No significant difference in the naphthalene metabolite profile occurs in the presence of Corexit 9527®. Degradation of naphthalene occurs in the absence of *Isochrysis galbana* indicating the formation of metabolite products are the result of photo-, bacterial, or other degradation pathways.

## INTRODUCTION

When crude oil is accidentally released into the ocean it threatens all levels of marine life. Crude oil consists of numerous compounds, whose chemical properties (water solubility, vapor pressure,  $K_{OW}$ ) in combination with physical conditions present at the site of the spill, dictate their environmental fate. The toxicity of petroleum hydrocarbons is well documented (Evans and Rice 1974; Whitman *et al.* 1984) in literally volumes of published research. Many variables are involved in determining the rates and endpoints of oil toxicity. Factors such as temperature (Korn *et al.* 1979), salinity (Linden *et al.* 1979), pH and route of exposure (Lee *et al.* 1976) may effect bioavailability and toxicity, while an organism's species, sex, and stage of development at the time of exposure may be critical in determining the effect of the toxic insult (Varanasi *et al.* 1989).

The primary components, petroleum hydrocarbons, represent a variety of aliphatic and aromatic compounds with a broad spectrum of toxicity. Of primary concern are the aromatic hydrocarbons, both mono- and polycyclic, which may be mutagenic, carcinogenic, or neurotoxic. For surficial spills, the monocyclic aromatics (e.g., benzene, toluene, and the xylenes) may not represent a serious threat, as while they are relatively water soluble, they also possess high vapor pressures and rapidly volatilize. However, for benthic spills (such as leaks from ruptured pipelines and sunken ships), petroleum hydrocarbon exposure to pelagic communities may occur prior to rising to the surface for evaporation. The polycyclic aromatics, possessing low vapor pressures, tend to remain near the surface following a spill. While having relatively low water solubilities, they may represent the largest and most toxic aromatic component in the water column.

Other organics, such as the wide variety of both straight chain and branched aliphatic hydrocarbons present in all oils, represent a smaller proportion of the water accommodated fraction due to their inherent low water solubilities. Due to their low vapor pressures, they tend to remain at the surface and form the bulk of an oil slick. Their toxicity tends to be low; they are mainly neurotoxic (causing nonspecific neuropathies), and also act by physically coating organisms, disrupting cellular osmotic regulation.

Additional compounds include oxygenated organics, such as phenols, and various metals, such as arsenic (as arsenate). Both general classes tend to be highly toxic due to their ability to disrupt cellular respiration via the inhibition or uncoupling of mitochondrial oxidative phosphorylation. While their concentrations tend to be very low, their high toxicity compensates. They are also very water soluble and easily enter water column following an oil spill. Because of this movement into pelagic communities, these petroleum hydrocarbons may be responsible for a significant amount of mortality following a spill event.

An important issue to be addressed is the means of dispersion of oil following a spill. Methods to enhance the degradation of oil have been met with limited success due to the complex

composition of crude oil, the presence of numerous types of petroleum hydrocarbons, and their characteristic physical properties. Natural mechanical dispersion and biodegradation may be limited to compounds with high vapor pressures or high water solubilities (Cerniglia and Heitkamp 1989; Thomas *et al.* 1986). An alternative method, the use of oil dispersants or surfactants, The use of chemical dispersants on oil spills offers the benefit of reducing, perhaps even eliminating, the threat of oiling shorelines and surface inhabitants such as marine mammals and seabirds. While these benefits are clear to all, questions remain concerning the immediate and long-term fate of the dispersed oil in marine environment. By increasing aqueous concentrations of petroleum hydrocarbons through solubilization or emulsification, degradation is enhanced (Tiehm 1994), while the portion of crude oil in the water column that is available for uptake by organisms, the *bioavailable* fraction, is also increased. Further, the dispersing agent may enhance bioavailability as a result of altered interactions between dispersed petroleum hydrocarbon droplets and organismal cell membranes.

At an acute level the use of chemical dispersants in clean-up efforts raises a number of concerns; the toxicity of the dispersant product itself, the toxicity of increased dispersant facilitated concentrations of petroleum hydrocarbons in the water column, and the combined toxicity of dispersant and petroleum hydrocarbons. Studies indicate dispersants alone are more toxic than the oil they disperse and the effectiveness of a dispersant may directly correlate with its toxicity (Bratbak *et al.* 1982). Dispersing agents produce tissue damage and alter sodium regulation in rainbow trout (*Oncorhynchus mykiss*; McKeown and March 1977), and cause tissue disintegration and chemoreceptor damage in yellow bullhead (*Ictalurus natalis*; Bardach *et al.*, 1965). Exposing rabbit fish (*Siganus rivulatus*) to 10 ppm concentrations of dispersant alone produced a greater reduction in blood hematocrit than exposure to 10 ppt concentrations of crude oil alone (Eisler, 1975). In marine phytoplankton, growth rate inhibition has been observed with a variety of species (Portmann 1972; Tokuda and Arasaki, 1977, and Harrison *et al.* 1986).

Consequences of increased bioavailability could include increased bioaccumulation and changes in metabolic disposition, resulting in increased toxicity either directly or through the food chain. To date, little information is available on the sub-lethal effects of dispersants their role in the bioavailability and disposition of petroleum hydrocarbons in marine food chains.

The combined effects of petroleum hydrocarbons and dispersant toxicity have been addressed to a more limited extent, emphasizing acute toxicity.  $TL_{50}$  studies indicate an increase in the toxicity of oil when dispersant has been applied, however, a broad range of toxicities exist among the dispersants tested (Thompson and Wu 1981).

Limited research to date has emphasized the biological fate of sub-lethal concentrations of petroleum hydrocarbons and the influence dispersants may have on these pathways. Understanding bioavailability and disposition of these compounds in aquatic organisms is critical in determining the

environmental fate of spilled oil. Most of the petroleum hydrocarbons that enter the aquatic environment will ultimately be transformed and degraded through physicochemical degradation such as photodegradation and biodegradation pathways which occur in microorganisms, animals, and plants. These biodegradation processes remove the parent compound, based on its bioavailability, from the environment replacing it with products of varying toxicity.

Bioavailability is thus the extent to which receptor sites on and within an organism interact with a compound and can be quantified in terms of bioaccumulation (Zakrzewski 1991). Exposure is the result of a chemical crossing a biological membrane and bioaccumulation occurs when the rate of uptake exceeds the rate of elimination-- $K_{\text{uptake}} > K_{\text{elimination}}$ . Uptake and bioaccumulation are both evident in primary levels of marine food chains. Freshwater and marine microalgae, primary producers, have been shown to rapidly accumulate high concentrations of petroleum hydrocarbons during exposure to low concentrations in the ambient medium. Studies also show marine and estuarine copepods (Harris *et al* 1977) and the rotifer, *Brachionus plicatilis* (Echeverria 1980), all primary consumers, to accumulate petroleum hydrocarbons from chronic low level exposures. Studies with Pacific herring, like many small and larval stage fish, both a primary and secondary consumer, showed substantial accumulation of two of the most abundant petroleum hydrocarbon components of the water accommodated fraction (WAF) of oil, benzene and toluene (Korn *et al* 1977). The bioconcentration factor (BCF) refers to the relative distribution of a compound between sea water and an organism and usually directly relates to its octanol-water partition coefficient ( $K_{\text{ow}}$ ; Mackay 1982). While  $K_{\text{ow}}$  and BCFs are known for many of the constituents of petroleum, no studies to date have examined how dispersants alter BCFs in these primary levels of marine food chains.

The disposition of a compound upon entering an organism is determined by the absence or presence of systems that can metabolize or transform it. Depuration occurs as compounds are excreted either unchanged or after metabolic transformation by an exposed organism. Characterizing the depurate in terms of its components (parent and metabolite) and their relative abundances can provide valuable information. Since bioaccumulation is the net result of  $K_{\text{uptake}}$  from all routes-- $K_{\text{elimination}}$ , the rate of elimination could increase with the rate of uptake and there would be no observed increase in bioaccumulation. However, in both uptake and elimination there would have to be increases in the cellular activity involved with xenobiotic transport and transformation, both potentially energy demanding processes. Changes in depurate composition identify possible exposure interactions (both activation and inhibition) with metabolic pathways. Evidence of altered metabolic pathways provides information concerning enzyme systems sensitive to oil-dispersant exposure. Any factors effecting these systems could potentially alter the amount of bioaccumulation or metabolic profile within an organism.

To date, the vast majority of petroleum hydrocarbon studies have focused on macroinvertebrates and fish. While these species are of primary commercial concern, it would seem a great oversight to neglect those species at lower trophic levels on which they are dependent. A typical marine food chain consists of phytoplankton, primarily diatoms and dinoflagellates as primary producers, followed by zooplankton, as primary consumers, ranging from microinvertebrates to larval forms of larger species. Secondary consumers would include macroinvertebrates and adult fish species and subsequently marine birds and mammals. Phytoplankton are widely distributed in the marine environment and because of their limited mobility have little ability to escape stresses such as an oil spill, thus organisms like *Isochrysis galbana* play an important role in determining the fate of hydrophobic organic compounds in aquatic systems. The lipid rich composition of algae is a chemically suitable medium to receive hydrophobic moieties from sea water. Dead algal cells with their lipid storehouses of hydrophobic organic compounds fall to the ocean floor where they either decompose and become part of the bottom sediment, or they can enter the food chain when they are consumed by detritivores. While alive, algal cells are eaten by grazing zooplankton which also provides entry to the food chain. The degree to which a particular pathway is followed depends on primary production rates, grazing rates, and consumer abundance; yet, it has been determined that the majority of algal carbon makes its way into higher trophic levels (Swackhamer and Skoglund 1993). Consequently, any increase in bioaccumulation at the phytoplankton level could increase exposure to higher trophic levels risking reduced productivity or elimination of important marine resources.

The California Department of Fish & Game's Office of Oil Spill Prevention and Response (OSPR), the Marine Spill Response Corporation (MSRC), and the University of California currently support ongoing research at our lab investigating the effects of spilled oil and dispersants on marine resources. Studies cofunded by the US Coast Guard focused on changes in the bioavailability of petroleum hydrocarbons to primary levels of the marine food chain in the presence of chemical dispersing agents. This research program, designed to elucidate the influence of dispersants on the environmental fate of petroleum, focusing on uptake, bioaccumulation, and metabolic fate within primary levels of marine food chains, should be helpful in guiding oil spill cleanup and remediation efforts.

The specific objectives addressed in this report are: 1) the development of methods for the preparation, analysis, and characterization of PBCO WAF and chemically dispersed (using Corexit 9527®) PBCO; 2) the development of methods for the collection, separation, identification, and quantitation of the model hydrocarbon, naphthalene and its breakdown products; 3) experiments to determine changes in uptake and bioconcentration of naphthalene by *Isochrysis galbana* from WAF and DO preparations; 4) experiments to determine changes in naphthalene metabolite formation in *Isochrysis galbana* exposed to WAF and DO preparations.

## **MATERIALS AND METHODS**

**OBJECTIVE ONE:** The development of methods for the preparation, analysis, and characterization of PBCO WAF and chemically dispersed (using Corexit 9527®) PBCO (DO).

In order to pursue studies of the bioavailability of petroleum hydrocarbons with any consistency, it was first necessary to develop and optimize a method to create a reproducible water accommodated fraction of crude oil and dispersed oil exposure media. The primary objectives of this phase of the project were to determine an appropriate application rate to deliver the maximum concentration of hydrocarbon while not producing overt toxicity in algal cultures. Once the application rate was determined through a series of population density studies, a simple characterization of the exposure media was run to determine basic composition and to quantify the concentration of naphthalene, the model hydrocarbon, in this preparation.

### **PRIMARY COMPONENTS**

The model crude oil used was PBCO (EPA Standard, RT Corporation, Cheyenne, WY). Since the spill in Prince William Sound, much attention has been focused on Prudhoe Bay and the Alaskan North Slope, the largest oil producing region in North America. Along the Pacific Coast of North America, PBCO is the most heavily transported crude and thus statistically the most likely to be involved in a spill.

The model dispersant was Corexit® 9527. Of the many dispersants manufactured all are surfactant-based products. After polling oil spill responders in California, Corexit® 9527, manufactured by Exxon Chemical Co, Houston, TX, emerged as the most widely stockpiled dispersing agent.

The primary producer in the study was the golden brown algae, *Isochrysis galbana*, a commonly cultured, unicellular, photosynthetic algae. This organism is found in both marine and estuarine habitats and is of economic importance as the primary food source for larval stages of commercially and recreationally significant fish species harvested along the Pacific Coast.

### **METHODS**

#### **Preparation of WAF and DO Exposure Media**

WAF preparation methods were developed from early methods utilized by Michael Singer at the Granite Canyon Laboratory, UCSC.



Exposure media was prepared with filtered sea water (34 ppt salinity) obtained from the Long Marine Laboratory, University of California, Santa Cruz, California and stored at 4°C. Sea water was filtered twice through a 0.2 µm filter (MSI, Westboro, MA) and used directly for 34 ppt media or diluted with Nanopure® (Barnstead, Dubuque, Iowa) water to 22 ppt salinity for brackish media. The WAF exposure media was prepared by weighing 22 or 34 ppt water into 2 L aspirator bottles (Fisher Scientific, Pittsburgh, PA) outfitted with a glass spigot, a Teflon stopper, and a magnetic stir bar. PBCO was then weighed on to the top of the water using a glass pipette. The DO preparation was prepared in the same fashion with the addition of Corexit® 9527 at a rate of 10 µl/g of crude oil using a variable volume micropipet (Oxford, St. Louis, MO). The bottles were covered with aluminum foil to eliminate the risk of photodegradation. The bottles were placed in the cold room at 20°C and spun at 200 rpm on electromagnetic stir plates (LTE Scientific, Oldham, UK) to ensure consistent mechanical input in each preparation. Samples were collected at various timepoints by stopping stirring and removing 10 ml of "waste" through the glass spigot located before drawing the actual sample. More than 2/3 of the total volume was never removed to avoid disturbing the excess oil on the surface.

#### Determining Loading Rate

WAF and DO exposure medias were prepared at both salinities using three different loading rates. Seawater (34 ppt) and brackish water (22 ppt) was weighed (2000 g) into the aspirator bottles. PBCO was weighed in on top at rates of 1, 2, and 10 g/L or 2, 4, and 20 g, respectively. For DO preparations, 10 µg/g PBCO was added to the center of the oil, or 20, 40, and 200 µg, respectively. Bottles were covered and set to stir in the coldroom. Samples were collected at 1, 2, 4, 8, 12, 24, and 48 hour time points and analyzed directly for total carbon content using a Rosemount-Dohrmann DC-190 TOC Analyzer (Santa Clara, CA). All samples were run in triplicate.

#### Selecting an Exposure Concentration

Inoculating cultures of *Isochrysis galbana* were obtained from culturing facilities located within the Long Marine Lab, UCSC. Large scale production of *I. galbana* was integrated into existing facilities at the UCSC Environmental Toxicology cluster drawing from culturing techniques practiced by researchers at the Los Angeles County Museum of Natural History-Southern California Edison's Redondo Beach Laboratory.

Organisms were batch cultured in double filtered (0.2 µm), autoclaved 34 and 22 ppt water in polyethylene foam stoppered Erlenmeyer flasks. F/2 nutrient (Fritz Aquaculture, Dallas, TX) was added to all cultures and exposure media at manufacturers' prescribed quantities. Coldroom conditions were maintained at 16°C with a 16 hour light:8 hour dark photoperiod. Subsequent

transfers to larger containers were done at appropriate cell densities, to a final 20 liter carboy. Air was bubbled through cultures using a Whisper 800 aquarium pump (Oakland, NJ). Cultures used in all exposure studies were in mid- to late-exponential growth phase with approximately 1.5 to 2 million cells per milliliter of culture.

Preliminary exposure studies were run with varying loading rates of PBCO (1, 2, and 10 g/L) in the 24 hour WAF and DO preparations. WAF and DO preparations at both salinities were evaluated for overt toxicity by placing three parts of algae culture to one part of exposure media in a polyethylene foam stoppered Erlenmeyer flask. Controls were run with three parts of algae culture to one part culture media. F/2 nutrient was added as needed. Exposure studies were run in a 16°C coldroom with a 16 hour light:8 hour dark photoperiod for 96 hours. Samples were drawn at 24 hour intervals and counted for population densities.

Subsequent studies were done using the same format with varying dilutions of the three loading rate WAF and DO preparations. Using 100% to denote a preparation directly from the aspirator bottle, dilutions were prepared using 50 and 25% volumes of WAF and DO with the balance made up of culture media, ie, a 50% exposure consisted of 3 parts algal culture and 1 part consisting of half WAF or DO and half culture media.

Based on the results of previous experiments, the concentration with the maximum loading of petroleum hydrocarbon and no observed changes in population density was selected. The final study was run with three parts algal culture in early stationary phase (4-6 million cells/ml) and one part 2g/L WAF and DO preparation at 100% concentration over a five day period. Samples were taken and counted and compared to controls.

#### Characterization of WAF and DO Preparations

Studies were run to determine the composition of the 2 g/L WAF and DO preparations in terms of naphthalene, the model hydrocarbon, total petroleum hydrocarbon, and a simple characterization of its composition. WAF and DO were prepared using methods previously described. During the 48 hour stirring period 500 ml samples were collected at 2, 4, 8, 12, 24, and 48 hour timepoints. All timepoints were run in triplicate. Blanks were run with 22 and 34 ppt water. Each sample was vacuum extracted onto a 6 cc, 1 g octadecylsilane (C<sub>18</sub>) solid phase extraction (SPE) cartridge (Varian, Harbor City, CA). Cartridges were conditioned with 5 ml of ethyl acetate followed by 5 ml of deionized water. As the last of the water passed through the cartridge the sample was added. After the last of the sample had passed through the cartridge, it was vacuum dried for approximately 60 seconds. The sample was eluted from the cartridge with 5 ml of ethyl acetate.

Samples were analyzed by a Hewlett Packard (Palo Alto, CA) 5890A gas chromatograph (GC) fitted with a 7673A autosampler, flame ionization detector (FID), and a 60 m x .25 mm ID

(.25  $\mu\text{m}$  film thickness) DB-5 glass capillary column (J&W Scientific, Folsom, CA). The temperature program for WAF analysis consisted of an initial temperature of 29°C with a 10°/min ramp to 150°C, holding for 1 minute, followed by a 6.5°/min ramp to 280°C with a five minute final hold. DO analysis had an additional 10°/min ramp to 325°C with an 18 minute hold. Injector and detector temperatures were 250 and 325°C, respectively. A 5 point standard curve was run with naphthalene prepared in ethyl acetate at concentrations of 10, 50, 100, 500 and 1000 ng/ $\mu\text{l}$ .

**OBJECTIVE TWO:** The development of methods for the collection, separation, identification, and quantitation of the model hydrocarbon, naphthalene and its breakdown products.

### **PRIMARY COMPONENTS**

The radio-labeled model petroleum hydrocarbon used was  $^{14}\text{C}$ -naphthalene (Sigma, St. Louis, MO), a polycyclic aromatic with a relatively low molecular weight and high water solubility. Naphthalenes, as a group, represent approximately 9.9% of the composition of PBCO (Thompson *et al.* 1971). Naphthalene was selected as a model petroleum hydrocarbon due to its presence in both crude and refined petroleum products, high toxicity, and because metabolite standards were readily available from chemical suppliers, greatly simplifying chemical analysis.

The isolation and concentration of naphthalene and its breakdown products was achieved using SPE techniques. Analytes collected were then fractionated and identified by HPLC co-chromatography methods using standards of  $\alpha$ - and  $\beta$ -naphthyl sulfate,  $\beta$ -naphthyl- $\beta$ -D-glucopyranoside,  $\alpha$ -naphthyl- $\beta$ -glucuronide, and  $\alpha$ - and  $\beta$ -naphthol obtained from Sigma. Quantitation was done using liquid scintillation counting (LSC).

### **METHODS**

#### Isolation and Concentration of Analytes

Methods were developed for the isolation and concentration of naphthalene and its metabolites, using SPE techniques. Initial experiments were run to optimize conditions including the selection of a disk or cartridge format; the best solid phase,  $\text{C}_8$  or  $\text{C}_{18}$ ; and the best solvent, acetonitrile, ethyl acetate, or methanol (Fisher Scientific, Fairlawn, NJ).

The first spike and recovery studies were run to select an SPE, bonded phase, and elution solvent for optimal retention of naphthalene. For each variable, a 4-liter amber glass bottle was filled with 4 liters of 22 or 34 ppt water. The water was spiked with  $^{14}\text{C}$ -naphthalene to a final concentration of 6 dpm/ml. One liter aliquots of sample were vacuum extracted onto each

conditioned SPE and vacuum dried for 60 seconds. Blanks were run with 22 and 34 ppt water. Samples were eluted from the SPE with the same solvent used in the conditioning step. All samples were run with a minimum of 3 replicates.

For SPE cartridges, a comparison was done of 6 cc BondElut® cartridges with 1 g of C<sub>8</sub> or C<sub>18</sub> solid phase material. Cartridges were attached to a vacuum manifold and were conditioned with approximately 5 ml (one void volume) of the eluting solvent, followed by 5 ml of deionized water. As the last of the water had passed through the cartridge, one liter of sample was added. A 60 second vacuum drying was used to remove any remaining excess water. Analyte was eluted from the cartridge by adding 2-3 ml of solvent to the cartridge and gently forcing it through the solid phase into a graduated test tube. An additional 2-3 ml of solvent was added to the cartridge and the process repeated to a total volume of 5 ml. The sample was then vortexed. Scintiverse LC (Fisher Scientific) was added to 0.5 ml of sample in a 7 ml scintillation vial, vortexed, and counted on an Beckmann LS6500 (Palo Alto, CA).

The comparison of SPE disks was done with 47 mm Empore® disks with C<sub>8</sub> or C<sub>18</sub> bonded phase. Disks were placed in a glass vacuum filtering flask set-up with stainless steel support (Fisher Scientific) and conditioned with 5 ml of eluting solvent followed by 5 ml of deionized water. As the last of the water passed through the disk, one liter of sample was added. The disk was vacuum dried for one minute. Solvent (5 ml) was placed in a 15 ml graduated conical test tube, the disk was folded and added to the solvent, and the tube was vortexed for one minute. scintillation cocktail was added to 0.5 ml of sample in a 7 ml scintillation vial, vortexed, and analyzed by LSC.

Based on the results of the first studies, spike and recovery experiments were run to determine the efficiency of C<sub>18</sub> 6 cc BondElut® SPE technique at recovering <sup>14</sup>C-naphthalene from the 2 g/L, 24 hour WAF and DO preparations. The same methods, as described previously, were used with ethyl acetate as the eluting solvent.

#### HPLC Separation of Naphthalene and Metabolites

HPLC techniques for the separation and fractionation of naphthalene and its metabolite products were developed from the methods of Seaton and Tjeerdema, 1995. Individual standard solutions of naphthalene the six metabolites,  $\alpha$ - and  $\beta$ -naphthyl sulfate,  $\beta$ -naphthyl- $\beta$ -D-glucopyranoside,  $\alpha$ -naphthyl- $\beta$ -glucuronide, and  $\alpha$ - and  $\beta$ -naphthol, were prepared at 1 mg/ml concentrations in methanol. Injections (20  $\mu$ l) were made on a Hewlett Packard Model 1090 HPLC (Hewlett Packard) system outfitted with a 25 cm C<sub>18</sub> column (Alltech, Deerfield, IL), diode array detector (254 nm) and a Gilson FC 203 automated fraction collector (Middleton, WI). The retention times of the individual standards were determined by reverse-phase separation with a 0.1% acidified water:acetonitrile mobile phase gradient.

After determining the individual retention times, a standard was prepared containing all seven components. Injections were made on the HPLC and the mobile phase gradient program was manipulated to maximize the separation of the individual components of the mixture.

### Sample Analysis

HPLC co-chromatography techniques were developed to analyze for the seven  $^{14}\text{C}$ -labeled compounds of interest from exposure study generated samples. The method included the injection of 50  $\mu\text{l}$  of 1 mg/ml mixed standard solution with the injection of 450  $\mu\text{l}$  of radiolabelled sample, prepared by the SPE method, into a 500 $\mu\text{l}$  injection loop on the HPLC. Using the chromatography of the standard as a guide, fractions were identified and collected from corresponding peaks of interest. Quantitation of  $^{14}\text{C}$ -naphthalene and radiolabelled products was done by placing 0.5 ml of each fraction in individual 7 ml scintillation vials, adding Scintaverse LC, and reading on the LSC.

**OBJECTIVE THREE:** Experiments to determine changes in uptake and bioconcentration of naphthalene by *Isochrysis galbana* from WAF and DO preparations.

### **PRIMARY COMPONENTS**

Studies were run with *Isochrysis galbana* cultures exposed to WAF and DO preparations in temperature controlled, closed system chambers. The chambers used were one liter, water-jacketed reaction flasks that were modified by the scientific glassblower at UCSC. Modifications included addition of a ground glass leur joint with stopcock for a sampling port. Chambers were silanized to reduce the loss of  $^{14}\text{C}$ -naphthalene and other non-polar compounds due to adsorbance to glassware. Chambers were autoclaved prior to each run to limit bacterial contamination. Exposure temperatures were maintained with a circulating cooling system (Fisher Scientific).

All exposure studies were run with a total of five chambers. Each study consisted of one exposure media, WAF or DO, and one salinity, 22 or 34 ppt. Three of the chambers in each study contained algae, WAF or DO, F/2, and  $^{14}\text{C}$ -naphthalene. Another chamber was used as an algal control, consisting of algae, F/2, and culture media to dilute to the one liter volume. The final chamber was a radioactivity control or mass-balance control, consisting of WAF or DO, culture media, F/2, and  $^{14}\text{C}$ -naphthalene.

Chambers were attached to a wall mounted system of scaffolding using ring mounts. Magnetic stir plates were mounted below each of the chambers. Grow lights were mounted behind the chambers and attached to timers.

## **METHODS**

### Preliminary Uptake Studies

Simple short term static exposure studies, run under ambient conditions, were run without WAF or DO to determine the time to equilibrium. One part of exposure media prepared with culture media, F/2, and  $^{14}\text{C}$ -naphthalene, was added to three parts of algal culture in a one liter Erlenmeyer flask. Samples were prepared at both salinities, with and without dispersant. Contents were covered and swirled and left on the bench top. Samples (10 ml) were drawn at 1, 2, 4, and 8 hour intervals and centrifuged. The pellet was digested with Scintagel and counted using LSC.

### Chamber Studies

WAF and DO exposure media were prepared at 20°C, 24 hours before the exposure study was to be set-up, using the previously described method. A caged, Teflon coated, magnetic stirbar was placed in the bottom of the chamber. The circulating cooling system was set at 20°C and allowed to equilibrate.

Exposure media (250 ml) was added to each of 4 chambers and nutrient was added to a constant concentration. The activity of the spiking standard of  $^{14}\text{C}$ -naphthalene was determined by LSC and the volume necessary to produce one liter with a concentration of 5000 dpm/ml was spiked into the 250 ml of exposure media.

A time-zero cell count was done to determine that algal densities were between 1.5 and 2 million cells per ml. Algal culture (750 ml) was added to each of four chambers. Chambers were covered and sealed. Chambers received a 16 hour light:8 hour dark photoperiod with constant gentle stirring.

Samples, approximately 11 ml, were drawn through the sampling port with a 30 ml ground glass luer-tip syringe at 1, 2, 4, 8, 12, and 24 hour timepoints. A small portion was fixed in methanol for cell counting and 10 ml of sample was put in a silanized glass centrifuge tube. The sample was pelleted with 10 minutes of centrifugation using a table top ICE Clinical centrifuge (Fisher Scientific). The radioactivity in the supernatant was determined by LSC. The remaining algal pellet was transferred to a scintillation vial and digested with Scintagel (Fisher Scientific) in a Precision 25 (Chicago, IL) shaking water bath at 50°C for 6 hours. Algae associated  $^{14}\text{C}$  was quantified by LSC.

**OBJECTIVE FOUR:** Experiments to determine changes in naphthalene metabolite formation in *Isochrysis galbana* exposed to WAF and DO preparations.

### **PRIMARY COMPONENTS**

Exposure studies were run following the protocol discussed in Objective Three.

Naphthalene metabolite studies consisted of the SPE of exposure media from the previous studies, following centrifugation. Supernatant is extracted on SPE cartridges, eluted, and fractionated by HPLC co-chromatography. Identification of metabolites is done using known standards and the fractions are quantified by LSC. Pelleted cell material was digested with methanol and sonication and followed the same analysis steps as the supernatant.

### **METHODS**

Following the twenty four hour time point, exposure media was separated from algal cells by centrifugation. Sample material was weighed into 250 ml centrifuge tubes and balanced. Samples were spun for 15 min at 7500 RPM at 20°C on a Sorvall RC-5B Centrifuge (DuPont, Wilmington, DE). The supernatant was then extracted on a conditioned 6cc, 1 g, C<sub>18</sub> SPE cartridge. Sample was then eluted with 20 ml of methanol, followed by 20 ml of ethyl acetate. Eluate was injected on the HPLC along with standards using the methods previously described. All fractions were collected and counted by LSC.

Algal cells were transferred to a glass graduated conical test tube and diluted to 9 ml with methanol. Tubes were capped and sonicated for 10 minutes to disrupt cells. Tubes were then centrifuged for 10 minutes using the ICE bench top centrifuge. Supernatant was injected with standards on the HPLC and analysis methods were the same as those used for supernatant.

### **RESULTS**

**OBJECTIVE ONE:** Preparation, analysis, and characterization of WAF and DO exposure media.

#### Determining Loading Rate

The effects of increasing loading rates (1, 2, and 10 g/L) are limited in WAF preparations (Figure 1.). At both the 1 and 2 g/L rates, total carbon content has come to equilibrium or saturation at approximately 24 hours with a concentration of 8-10 ppm (mg/L). At the 48 hour time point, the samples are all clustered around 10 ppm. At the higher loading rate (10 g/L), the total

carbon content has approximately doubled to 20 ppm by the 24 hour equilibrium time point. This is no difference between the total carbon concentration in the 22 and 34 ppt preparations.

In the DO preparations (Figure 2.), results for the lower, 1 and 2 g/L preparations, showed an approximate doubling of the total carbon concentration equivalent to the increase in loading rate. Again, equilibrium was reached by the 24 hour time point. At 48 hours the concentrations remained stable. Again, no variation was seen between the two salinities at these loading rates. At the higher loading rate (10 g/L) the total carbon concentration has increased by two orders of magnitude over lower loadings. Final concentrations at 24 hours showed a twenty percent difference in total carbon concentration between the two salinities, with 34 ppt having a concentration of 1200 ppm.

### Selecting and Exposure Concentration

Initial studies of overt toxicity with 1, 2, and 10 g/L loading rates of PBCO in WAF and DO preparations showed a high level of toxicity, particularly in the presence of dispersant. Virtually all cells were killed in the 10 g/L exposures. At lower concentrations, population densities in exposed cultures varied little from concentrations in controls.

Studies done with dilutions of WAF and DO preparations gave similar results at lower loading rates (1 and 2 g/L). Final results of the 96 hour 10 g/L dilution studies (Figure 3.) showed almost complete lethality at 50 and 100% concentrations in preparations with dispersant, with and without oil present. In 25% WAF and DO, exposed culture densities were equal to or greater than controls. In WAF exposures, 100, 50 and 25% concentrations yielded similar results, with exposed populations varying only slightly from controls.

Using the 2 g/L application rate as the final concentration for exposure studies, a confirmation study was run for a 5 day period. Results (Figure 4.) show that with a 100% preparation, population densities were not significantly different between exposed organisms and controls, at either salinity.

### Characterization of WAF and DO Preparations

The contribution of naphthalene, or native naphthalene in WAF and DO preparations of PBCO was determined with GC/FID analysis of samples concentrated on SPE cartridges. Back calculation to the original concentration in WAF and DO generated a 48 hour partitioning curve (Figure 5.). Equilibrium or saturation was reached by the 24 hour time point in WAF preparations with a native naphthalene concentration of approximately 250 µg/L in both salinities. Levels remained stable through the 48 hour time point. DO preparations showed greater variability, averaging 290 µg/L.



Total petroleum hydrocarbon data was generated in the naphthalene study but is only quantified in terms of the relative area counts. This information provided a partitioning curve (Figure 6.) similar to that of the naphthalene, with equilibrium attained by the 24 hour time point and stability through 48 hours.

Chromatograms of a 24 hour WAF and DO preparation (Figures 7a and 7b) show the differences in composition. WAF was dominated by monocyclics such as ethyl benzene and xylenes. DO, in addition to these constituents, had the characteristic alkane profile through C<sub>26</sub>.

***OBJECTIVE TWO: Collection, separation, identification, and quantitation of naphthalene and metabolites.***

#### Isolation and Concentration of Analytes

Results of the initial spike and recovery studies (Figure 8) showed a range of success in isolating and concentrating <sup>14</sup>C-naphthalene from aqueous preparations at 22 and 34 ppt salinity. In general, Empore® disk recoveries were lower than BondElut® cartridges for all phases and all solvents, ranging from 45 to 80%. Exceptions were the 22 ppt C<sub>18</sub> phase sample with methanol elution and the 22 ppt samples with acetonitrile elution from both C<sub>8</sub> and C<sub>18</sub> phases.

Cartridge recoveries for the C<sub>8</sub> were more consistent relative to each other, ranging between 80 and 90%. Results from C<sub>18</sub> studies using ethyl acetate as the eluting solvent were always the highest for both salinities, 92 to 98%.

The follow-up study (Figure 9.), run with WAF and DO preparations using C<sub>18</sub> BondElut® cartridges with ethyl acetate elution gave quantitative recoveries (>95%) in three out of the four samples. The exception, 34 ppt WAF showed good recoveries, 80% of the original <sup>14</sup>C-naphthalene spike.

#### HPLC Separation of Naphthalene and Metabolites

HPLC methods were developed for the separation of 7 compounds, parent naphthalene and 6 breakdown products (Figure 10). Optimized resolution of these 7 analytes of interest from a standard solution yielded the retention times (R<sub>t</sub>) shown in Table 1. The acidified Nanopure® water:acetonitrile gradient program used to achieve this separation is shown in Table 2. A sample chromatogram shows the optimized separation of the 7 compounds (Figure 11).

Table 1.  $R_t$  for Naphthalene and Metabolites

Compound	Retention Time (min)
$\alpha$ , $\beta$ -naphthyl sulfate	3
$\beta$ -naphthyl $\beta$ -D-gluco-pyranoside	8
$\alpha$ -naphthyl- $\beta$ -glucuronide	10
$\alpha$ , $\beta$ -naphthol	17
naphthalene	23

Table 2. Solvent Gradient

Time (min)	% Acidified H <sub>2</sub> O*	% Acetonitrile
0-5	80	20
6-11	70	30
12-17	50	50
18-23	40	60
24-29	30	70
30-35	20	80

\*0.1% acetic acid in Nanopure® water  
(flowrate-1.00 ml/min)

### **OBJECTIVE THREE:** *Changes in uptake and bioconcentration of naphthalene.*

#### Preliminary Uptake Studies

The time to equilibrium study indicated the majority of uptake occurred during the first four hours and came to steady state thereafter (Figure 12). Results are reported in dpm/10 ml of sample and are not corrected for population density. At both salinities, a marked inhibition of uptake occurs in the presence of the dispersing agent.

#### Chamber Studies

Results of the chamber studies (Figure 13) showed a similar trend to what was seen in the preliminary study in terms of inhibition of uptake in the presence of dispersant. The population density study was also run with the uptake data in this study, so results have been normalized to dpm/Cell for more accurate comparison. Data from the 22 ppt studies show that in WAF preparations the uptake of  $^{14}\text{C}$ -naphthalene by *Isochrysis galbana* is approximately 50% higher than uptake from DO preparations. Error bars indicate the standard deviation of the data set and show good close reproducibility between sample replicates.

A bioconcentration factor (BCF) was calculated from the dpm count of an experimentally determined 1 g wet mass sample of algae from the 24 hour sample divided by the dpm count of 1 g of exposure media at the 24 hour sample. The BCF for  $^{14}\text{C}$ -naphthalene in *Isochrysis galbana* exposed to the WAF media was 326, or 326 times more  $^{14}\text{C}$ -naphthalene was associated with the algae than the aqueous media. This compares to a BCF of 201 for  $^{14}\text{C}$ -naphthalene in the DO media, only 61% of the previous BCF.

#### ***OBJECTIVE FOUR: Changes in naphthalene metabolite formation.***

Metabolite formation results were broken into two graphs. The first (Figure 14.) shows the percent of the total recovered  $^{14}\text{C}$  material from either the extracted exposure media or the digested algae, that was in the parent  $^{14}\text{C}$ -naphthalene form. In all cases, the  $^{14}\text{C}$  that was associated with the algae cells was 100%  $^{14}\text{C}$ -naphthalene parent form. For the WAF and DO preparations at 22 and 34 ppt,  $^{14}\text{C}$ -naphthalene was between 75 and 85% of the  $^{14}\text{C}$  recovered. Error bars indicate the standard deviation of a group of three replicate studies.

The second graph (Figure 15.) shows the composition of the metabolite profile. No data is shown for the algal digests as 100% was  $^{14}\text{C}$ -naphthalene. For the remaining samples, the metabolite profile consisted of the 15-25% of the  $^{14}\text{C}$  and the products where it was incorporated. The  $\alpha$ - and  $\beta$ - naphthols dominated in all cases, followed by the  $\alpha$ - and  $\beta$ - sulfates. At much lower concentrations, < 1%, several conjugates were identified.

## **DISCUSSION**

#### ***OBJECTIVE ONE: Preparation, analysis, and characterization of WAF and DO exposure media.***

##### **Determining Loading Rate**

Results of the loading rate studies indicate that the effects of increasing loading concentration are not as critical in the absence of dispersant. By doubling the loading rate from 1 to 2 g/L there was little increase in the concentration of total carbon in the aqueous media. With a tenfold increase in loading there was only a doubling in total carbon concentration. This would suggest that the unfacilitated solubility of PBCO is very limited and even in the presence of a large volume of oil, the water is rapidly saturated. Although one would expect the lower salinity (22 ppt) preparation to have a higher concentration of total carbon based on a simple understanding of the

solubility of organics in salt solutions, no difference in the concentration of total carbon was seen between the two different salinities.

In the dispersed oil preparations, the effects of loading rate are more evident. A doubling in concentration of total carbon is seen with a double in loading rate, and a hundred fold increase is seen with only ten times the application rate. Clearly the presence of dispersant facilitates the solubility of petroleum hydrocarbons as anticipated. It is also notable, at the highest loading rate, the influence of salinity begins to play a role. Corexit 9527® was formulated for sea water salinity, 34 ppt, and is more efficient in solubilizing the oil at this salinity.

### Selecting and Exposure Concentration

Results of exposure studies helped to identify a concentration that would deliver the maximum concentration of hydrocarbon to the algae without evidence of overt toxicity. Initial exposures run with preparations from variable loading studies yielded range finding results. The 10 g/L loading rate was ruled out, due to almost total toxicity in the dispersed preparations. In order to have a comparative study, it was necessary for both preparations to come from the same loading rate, even though minimal evidence of toxicity was observed in the 10 g/L WAF.

To compare the effects of loading rate vs dilution, a series of dilution studies were run with the three different loading rates. At the 96 hour time point, no toxicity was observed in any of the 1 or 2 g/L WAF or DO preparations at either toxicity. At the 10 g/L concentration, preparations with dispersant were very toxic at 50 and 100% concentrations, but appeared to be a good energy source at the 25% concentration. Populations (22 ppt) exposed to the lower concentration of DO and dispersant only preparations had cell densities between 160 and 170% of controls. Population trends in all algae exposed to concentrations of 10 g/L WAF were similar to controls.

Based on the results of the dilution study, a 2g/L loading rate was selected. A 5 day exposure study run at this concentration showed no significant difference in population density between and exposed organisms. The 2 g/L loading rate was selected as the concentration to be used for the exposure studies.

### Characterization of WAF and DO Preparations

Results of the native naphthalene and simple characterization studies provided several important pieces of information necessary to proceed with the bioavailability studies. Based on the data collected the duration of WAF and DO preparation stirring was selected. In all four cases, both salinities and WAF and DO, a stable exposure media was obtained with 24 hours of mixing. Results from DO preparations consistently bounced back and forth within a narrow range, perhaps the result of individual droplets of oil present in these preparations limiting the chances of getting a homogeneous sample for analysis.

Total petroleum hydrocarbon data was also useful in demonstrating the differences in WAF and DO composition. DO preparations clearly had a greater number of constituents and increased concentrations of less soluble components. This would support the fact that dispersants preferentially interact with the compounds in oil with lower solubilities.

This fact is also supported by the results of the native naphthalene studies. It is notable that the concentrations of naphthalene only increase by approximately 10% in the presence of dispersant. Naphthalene is a relatively water soluble component of crude oil and consequently would move into WAF and DO unfacilitated.

Data from the native naphthalene study is also important in understanding how the addition of a radiotracer may alter the relative composition of WAF or DO. With naphthalene concentrations of 250-290 µg/L contributed by PBCO, the addition of 5000 dpm/ml of <sup>14</sup>C-naphthalene to exposure media, or 33 µg/L, represents 10% of the total.

***OBJECTIVE TWO: Collection, separation, identification, and quantitation of naphthalene and metabolites.***

#### Isolation and Concentration of Analytes

A method for the recovery of naphthalene and its metabolites was necessary to the overall project scheme. Solid phase extraction provided a simple, inexpensive, rapid method to remove analyte from bulk matrix without the expense, exposure, and waste management of organic solvents. SPE isolation and concentration steps were used to prepare samples for the analysis of any metabolic material found in the exposure media following algal exposures.

Empore® disk recoveries of <sup>14</sup>C-naphthalene routinely fell below those of cartridges, perhaps in part due to the increased surface area of the disk and opportunity for volatilization. Ethyl acetate elution provided the highest recoveries at both salinities in nearly all cases. Cartridges with C<sub>18</sub> solid phase were selected and yielded high recoveries in the subsequent matrix study.

#### HPLC Fractionation of Naphthalene and Metabolites

Degradation of naphthalene may yield a wide variety of products as a results of the processes available. Environmental factors, such as photodegradation, may play an important role in the breakdown of oil released at sea. Likewise, the presence of bacteria in seawater may help degrade naphthalene and form conjugates. A great deal of work has been done examining these and other pathways. Compounds selected for this study were identified as common breakdown products seen in the marine environment and represent only a few of the compounds potentially produced in aerobic and anaerobic degradation of naphthalene.

Gas chromatography methods are routinely a part of petroleum hydrocarbon analysis. For the purposes of the bioavailability studies, HPLC rather than GC techniques were selected for the fractionation of naphthalene and metabolic products for several reasons. Metabolites are often large or thermally labile molecules that fall apart at high gas chromatography temperatures. In addition, the recovery of volatile radiolabelled material following GC analysis would be problematic. The high water solubility of naphthalene metabolites makes them especially suitable for HPLC analysis.

The identification method described uses a 0.1% acidified Nanopure® water:acetonitrile mobile phase. The method was successful in separating the different compounds but not the  $\alpha$  and  $\beta$  isomers of the sulfates or naphthols. Subsequent results may indicate a mixture of these isomers. A confirmation method was also developed using a 0.1% acidified Nanopure® water:methanol mobile phase with C<sub>18</sub>. Separations were comparable to the acetonitrile results with the sulfates and naphthols remaining unresolved.

#### Sample Analysis

The use of co-chromatography methods provided a simple means to identify and quantitate trace levels of breakdown products generated during the exposure study

### **OBJECTIVE THREE: *Changes in uptake and bioconcentration of naphthalene.***

#### Chamber Studies

Results of both the preliminary and chamber studies indicate that the uptake of <sup>14</sup>C-naphthalene by *Isochrysis galbana* from 22 ppt WAF and DO preparations of PBCO is significantly inhibited in the presence of Corexit® 9527. As a result, the bioconcentration factor of 326 for WAF falls to 201 in the DO exposures. Results from the 34 ppt study was removed from the data sets due to an inconsistency. Further evaluation was necessary to determine statistical significance of findings.

The mechanism by which this reduction in uptake or association occurs is currently unknown but could possibly be the result of increased competition of <sup>14</sup>C-naphthalene with dispersant facilitated components of exposure media. Interactions between algal cell surfaces and dispersant may also play a role in reducing uptake either through disruptions of the cell membrane or physical association with surfactant molecules. Because of the lack of information on the mechanism it would seem prudent to further examine the issue before deciding this inhibition is a positive feature in the evaluation of dispersant use. Agents that act on surfaces, as dispersants are known to do, may inhibit the uptake of petroleum hydrocarbons but they also inhibit the uptake of nutrients necessary for the organisms survival. Disruption of the cell membrane may

symptomatically be observed as an inhibition in the uptake of petroleum hydrocarbons, but may have longer range effects, including loss of osmoregulation.

These endpoints may be of minimal concern in the evaluation of an isolated population of algae, but must be viewed more critically with subsequent higher trophic levels of the marine food chain.

#### **OBJECTIVE FOUR:** *Changes in naphthalene metabolite formation.*

Results of the metabolite formation studies were based on the total amount of  $^{14}\text{C}$  recovered in the different exposure studies. Metabolites were thus reported as a percentage of the recovered material. No significant variation occurs between the various exposure medias and the relative quantities and actual metabolites recovered. This would suggest that despite the changes in uptake observed in the previous study, there is no change in metabolic disposition of the material and no alteration in the breakdown pathways for  $^{14}\text{C}$ -naphthalene in *Isochrysis galbana* in the presence of dispersant.

Algae associated breakdown does not appear to occur, with all algae associated  $^{14}\text{C}$  being recovered in the parent  $^{14}\text{C}$ -naphthalene form. The presence of a metabolite profile similar to that of the supernatant was observed in the mass-balance control, exposure media without algae. This indicated that the formation of metabolites was likely the result of common bacterial and photodegradation pathways.

## **CONCLUSIONS**

Method development necessary to elucidate the answer to the question whether chemical dispersing agents influence the bioavailability of petroleum hydrocarbons to primary levels of marine food chains monopolized a substantial portion of the grant period. Based on the information acquired with the methods described, the following conclusions may be drawn. The presence of the dispersing agent, Corexit® 9527, significantly inhibited the uptake of  $^{14}\text{C}$ -naphthalene from DO preparations of PBCO by *Isochrysis galbana*. This was demonstrated in the 24 hour exposure study and supported by the changes in BCF in the presence of dispersant.

Metabolite formation in the presence of dispersant was the same as that observed in the WAF exposures, indicating that breakdown is occurring along similar pathways and in the same relative quantity.

Finally, the degradation of  $^{14}\text{C}$ -naphthalene observed in the absence of *Isochrysis galbana* indicated the formation of metabolite products resulting from photo-, bacterial, or other degradation pathways.

Continued studies will focus on the transfer of  $^{14}\text{C}$ -naphthalene from one trophic level to the next and determine the role of dietary versus aqueous exposure routes and how they may be influenced by the use of chemical dispersing agents.

## **ACKNOWLEDGMENTS**

The investigators would like to thank Gloria Blondina, Kim Gasuad, Eric Mielbrecht, Gerald Schwartz, Sara Singaram, Michael Singer, Jason Taylor, and Scott Udoff for their analytical and technical expertise. Thank you to Michael Sowby of the California Department of Fish & Game's Office of Oil Spill Prevention and Response for providing matching funds for this research.



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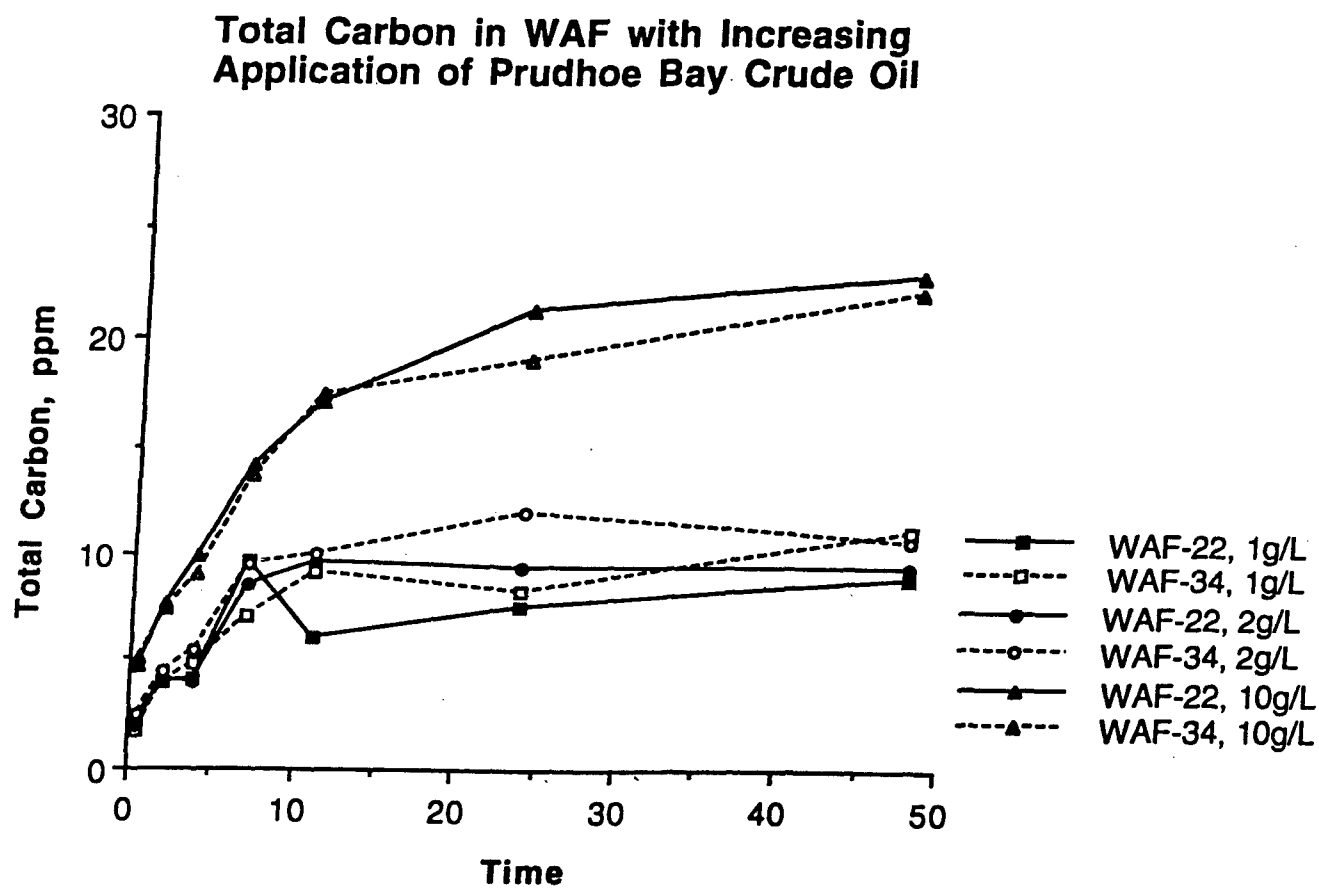
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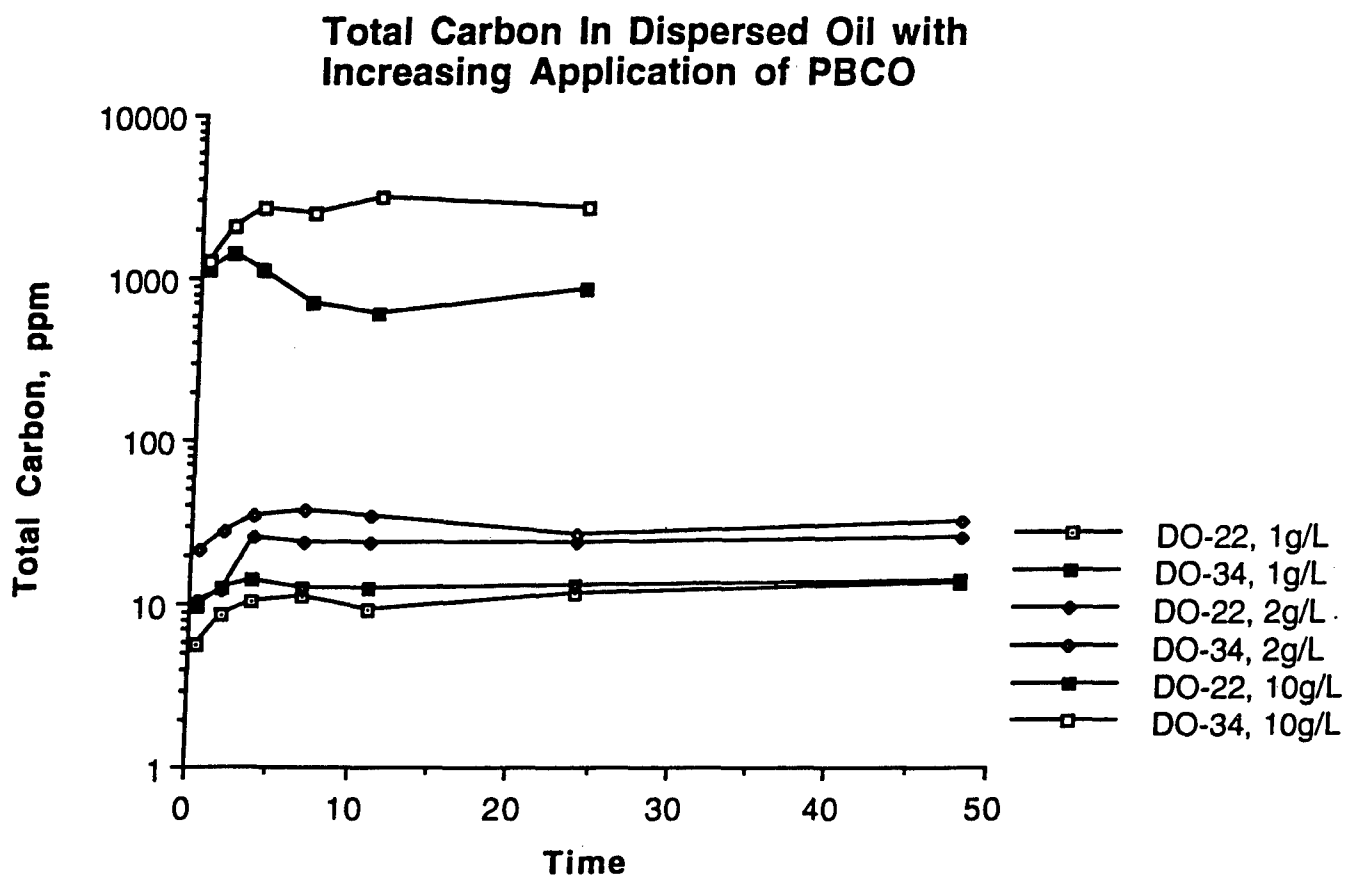
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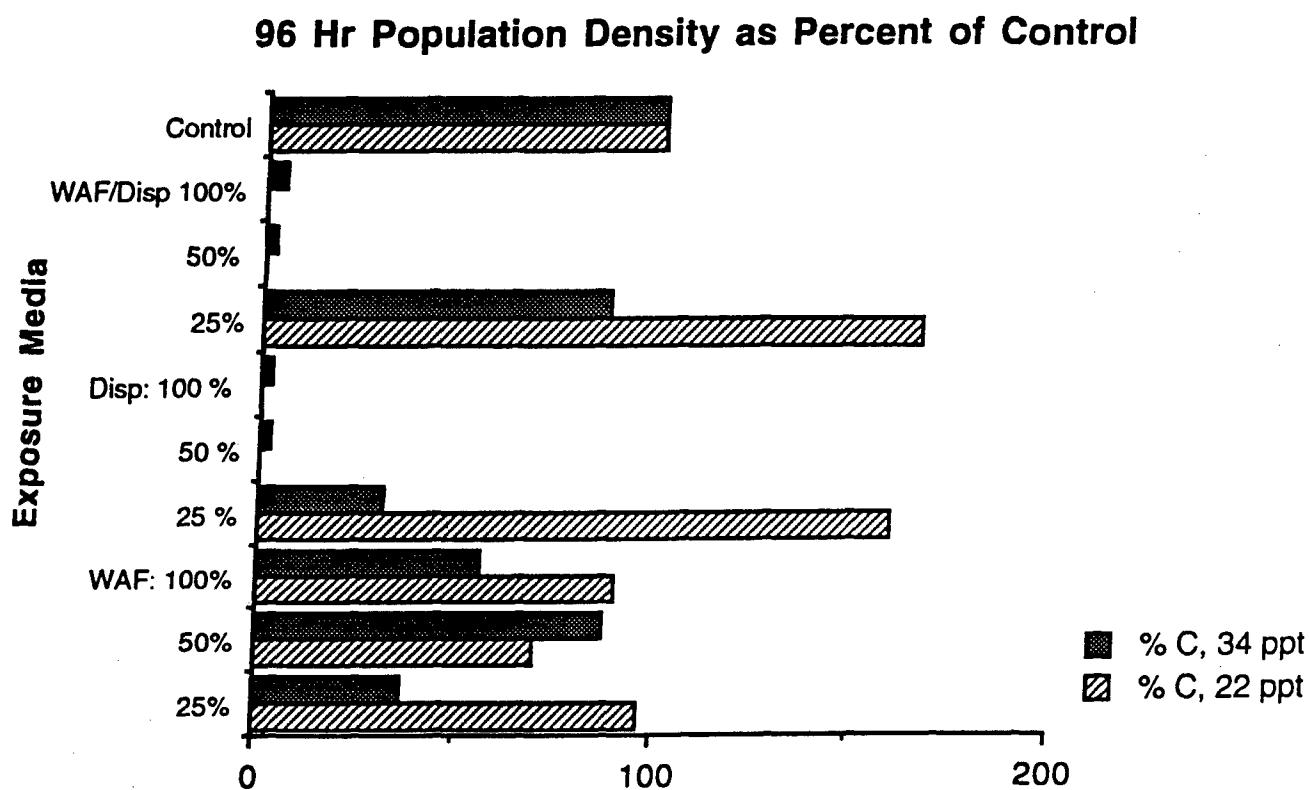
## APPENDIX



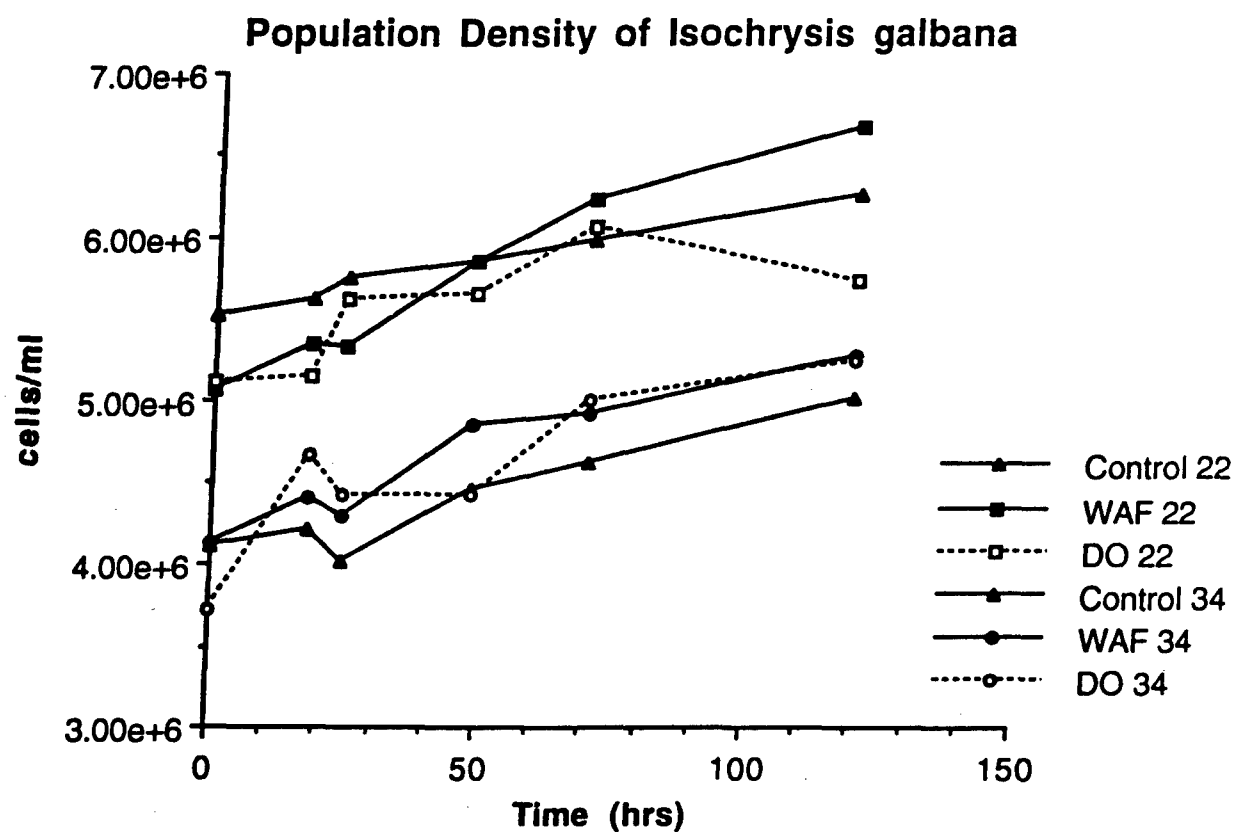
**Figure 1.** Effects of increasing loading rate on WAF composition.



**Figure 2.** Effects of increasing loading rate on DO composition.

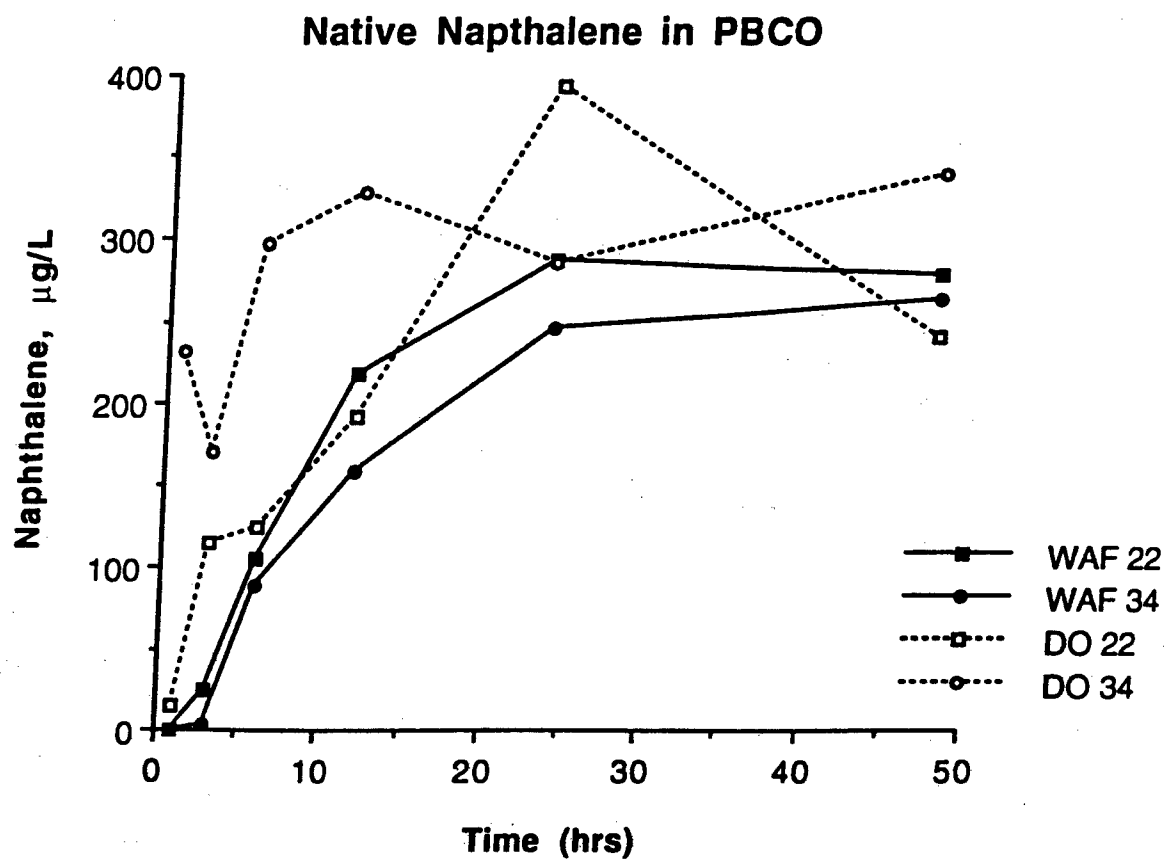


**Figure 3.** 96 hour WAF and DO population density studies

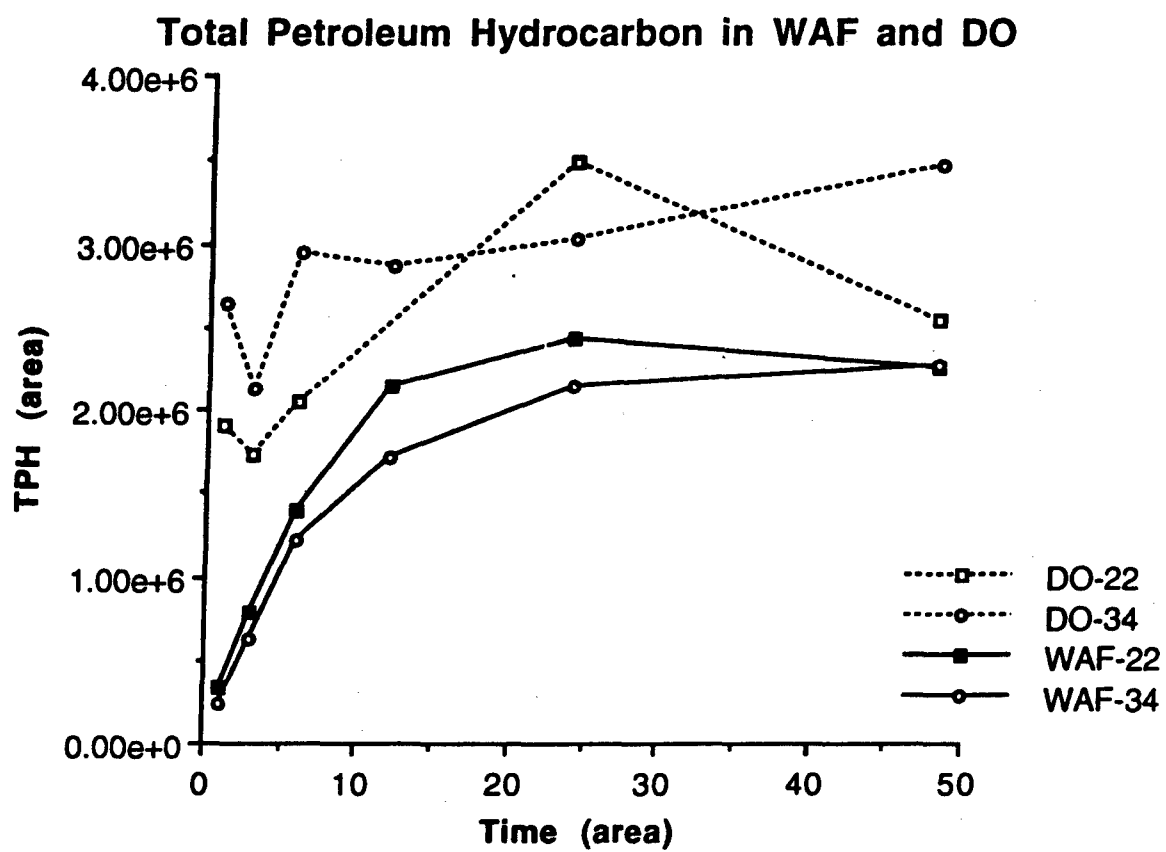


**Figure 4.** Population density study for 2g/L loading rate.





**Figure 5.** Native naphthalene in PBCO WAF and DO preparations.



**Figure 6.** Total petroleum hydrocarbon in PBCO WAF and DO preparations.

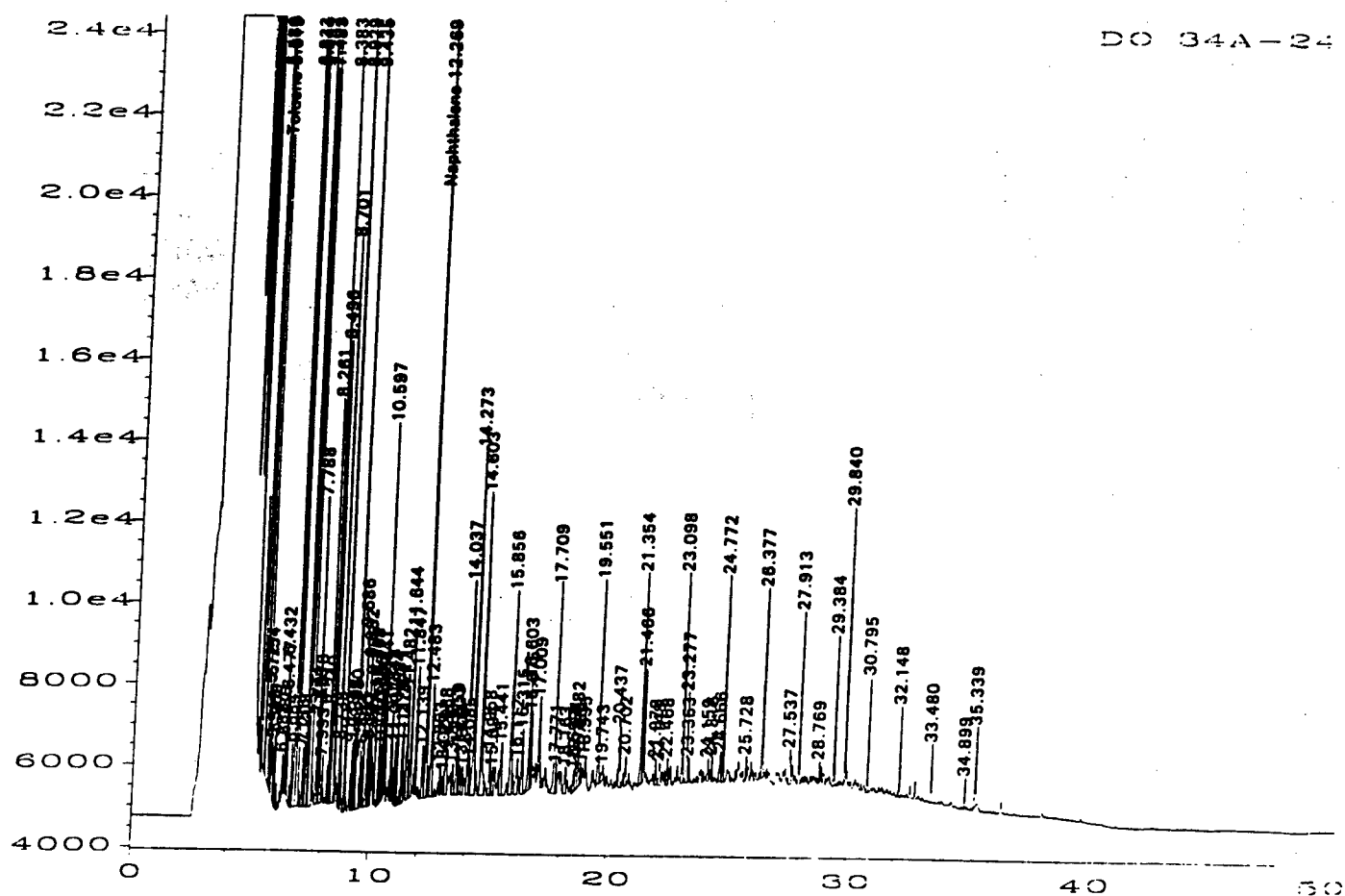
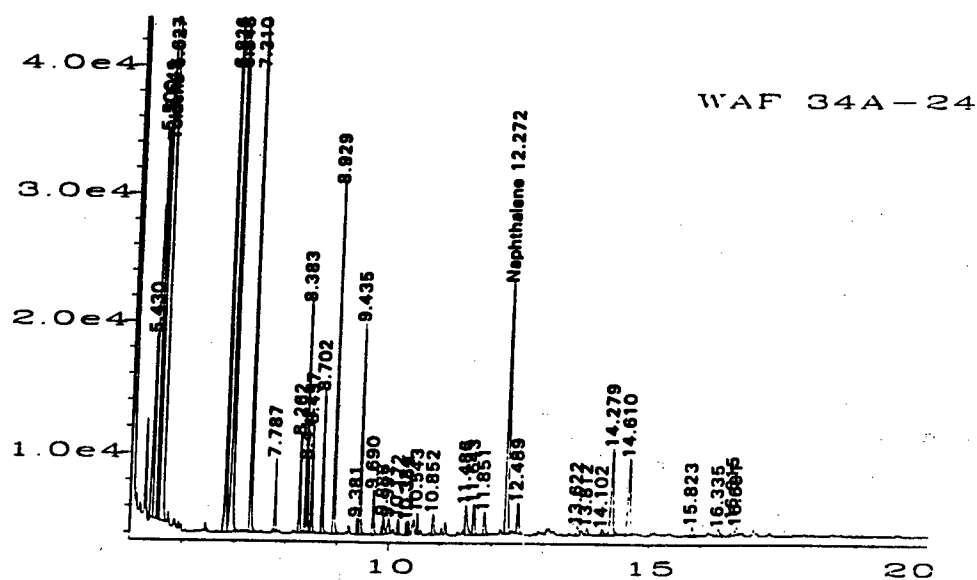
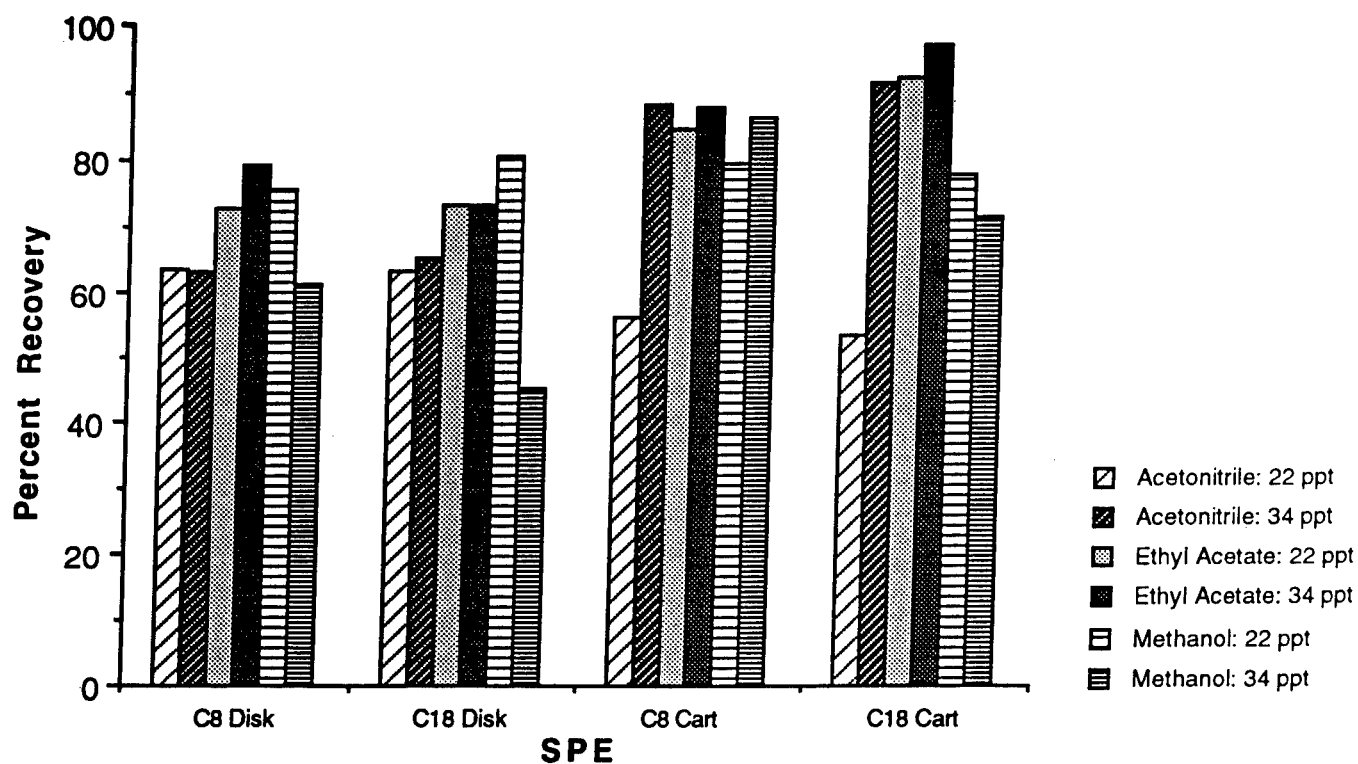


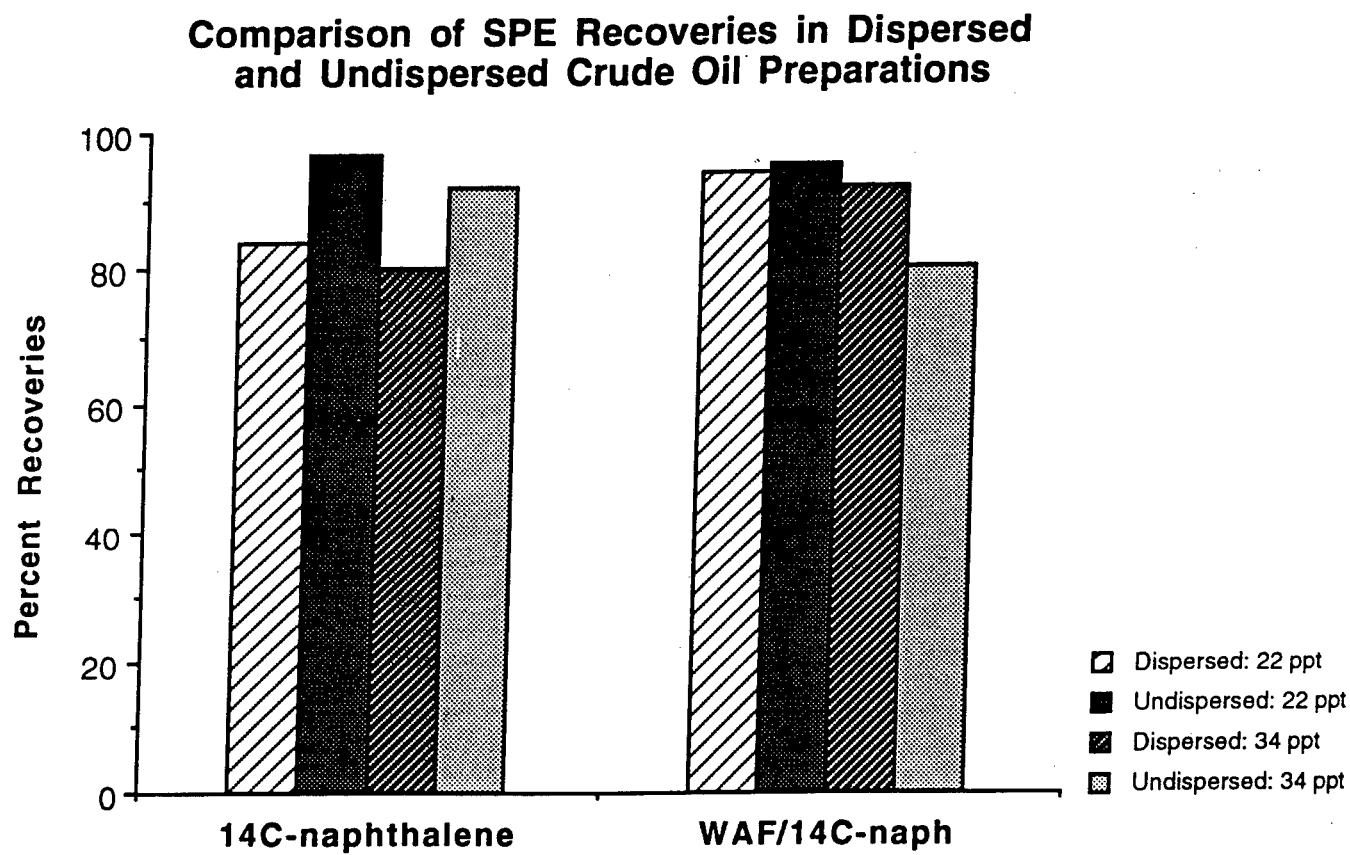
Figure 7a. GC/FID chromatogram of 34 ppt, 24 hour WAF preparation. (top)

Figure 7b. GC/FID chromatogram of 34 ppt, 24 hour DO preparation. (bottom)

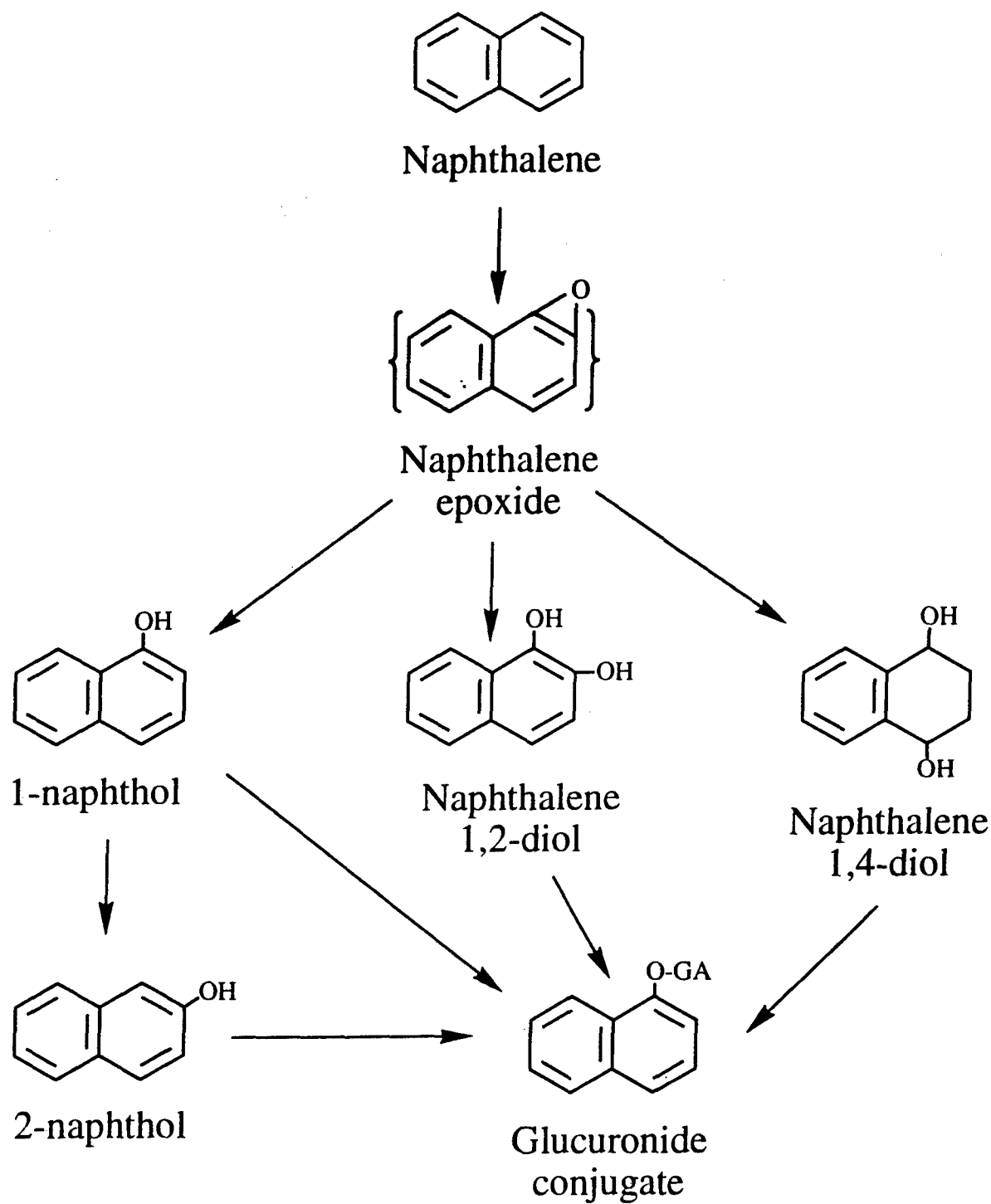
### Comparison of $^{14}\text{C}$ -naphthalene Recoveries



**Figure 8.**  $^{14}\text{C}$ -naphthalene recoveries using a series of SPEs and solvents.

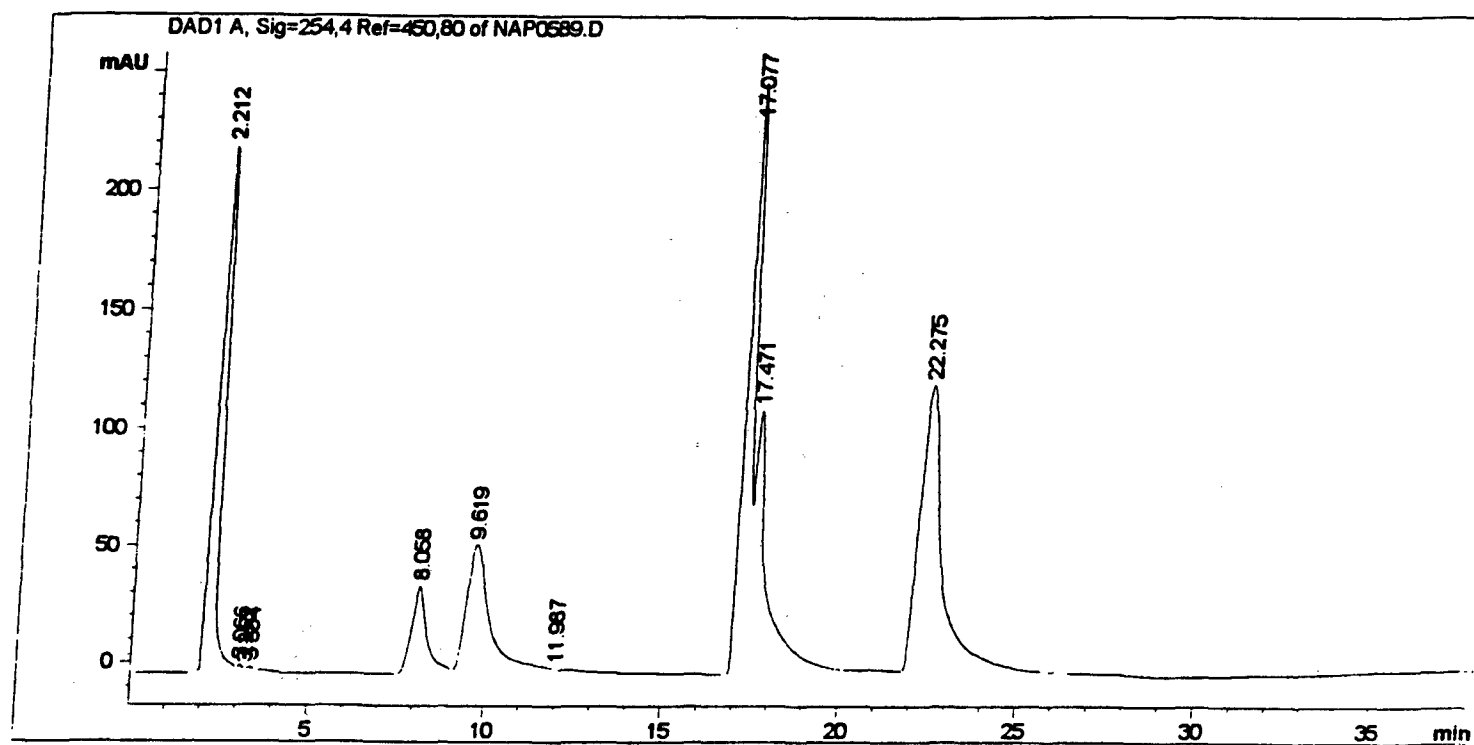


**Figure 9.** SPE recoveries of <sup>14</sup>C-naphthalene from WAF and DO.



## Naphthalene and Selected Metabolites

Figure 10.



**Figure 11.** HPLC chromatogram of naphthalene and metabolites.

### Static Uptake of Dispersed and Undispersed $^{14}\text{C}$ -naphthalene by *Isochrysis galbana*

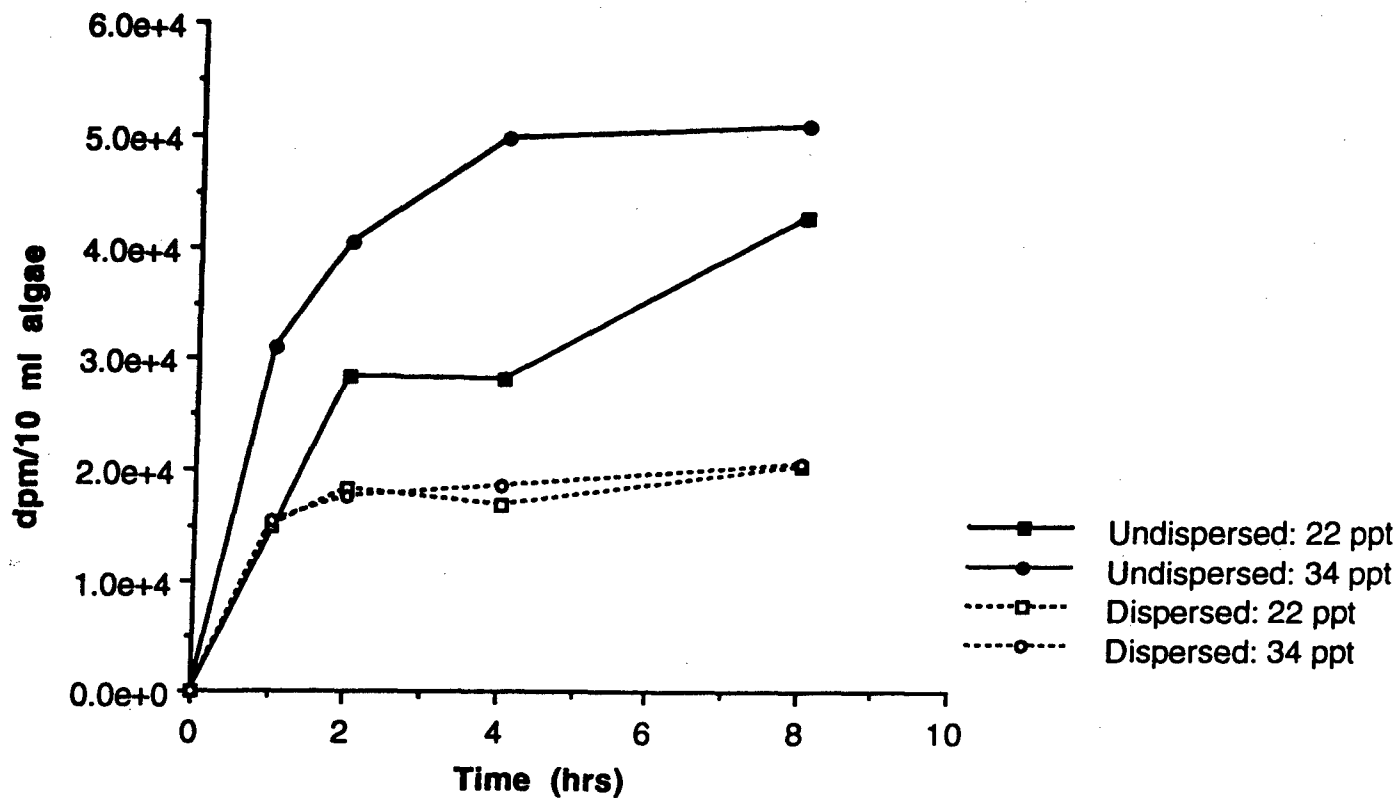
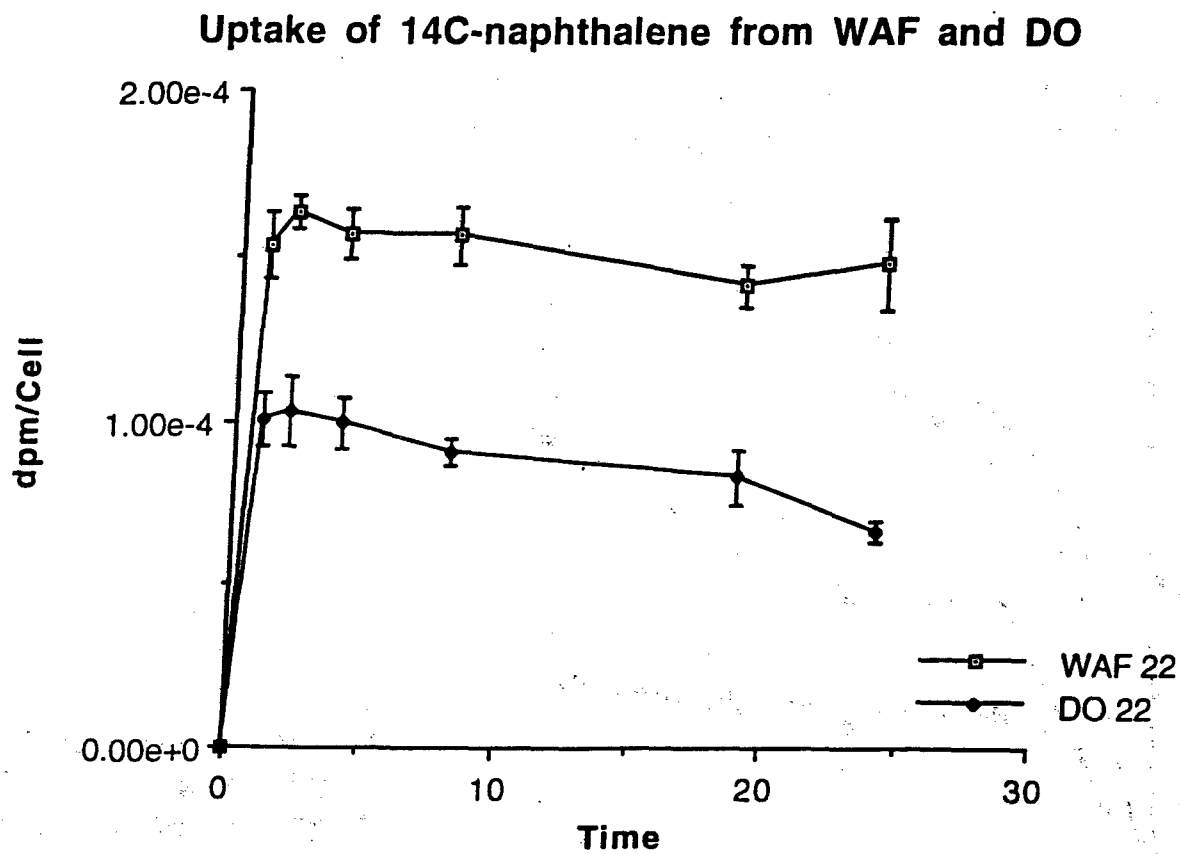
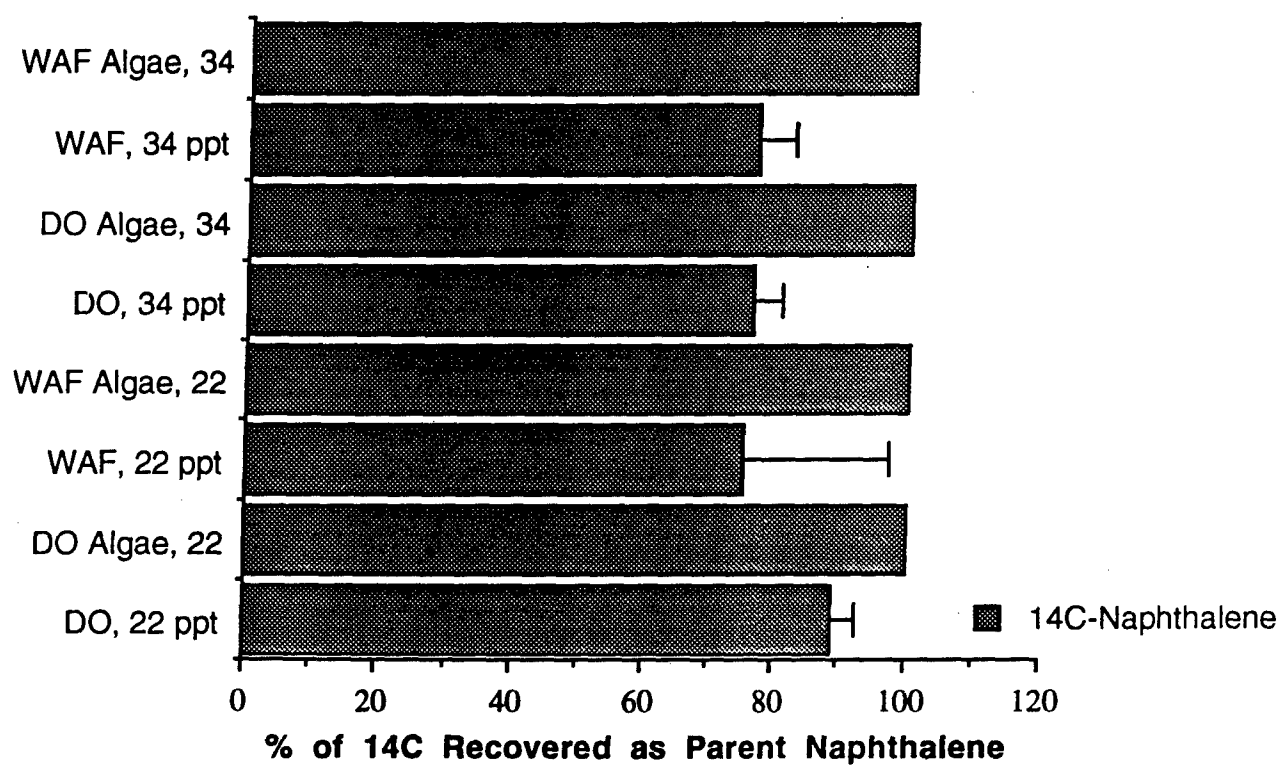


Figure 12. Static uptake of  $^{14}\text{C}$ -naphthalene by *Isochrysis galbana*.

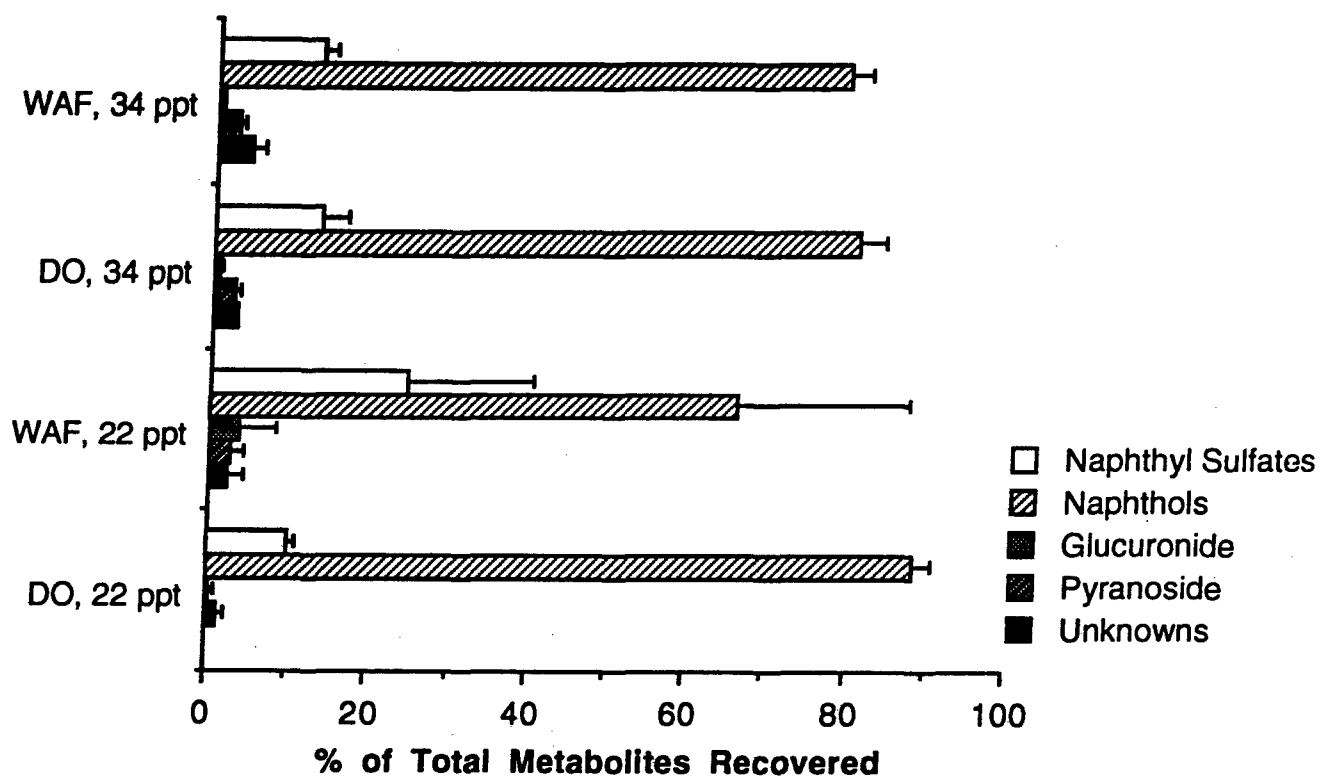




**Figure 13.** Uptake of  $^{14}\text{C}$ -naphthalene from WAF and DO exposures.



**Figure 14.**  $^{14}\text{C}$  recovered as parent naphthalene.



**Figure 15.** Profile of metabolites recovered.

## **PETROLEUM PC-BASED SHIPBOARD PILOTING EXPERT SYSTEM (SPES)**

*Martha Grabowski, Rensselaer Polytechnic Institute*

## EXECUTIVE SUMMARY

The PC-based Shipboard Piloting Expert System (SPES) project is aimed at developing a prototype PC-based version of the Shipboard Piloting Expert System (SPES). The project is implemented for a new piloting area - the St. Lawrence Seaway. The development platform selected is the Visual C++ programming language and a reasoning tool running on the Windows-NT operating system. The project is being implemented in phases, with Phase 1 focused on demonstrating the feasibility of the concept and Phase 2 focused on refining the prototype and building incremental functionality. The Phase 1 work, which was supported by an Oil Pollution Act of 1990 (OPA-90) Research Grant DTRS-57-94-G-00077, is reported on in this document.

The navigational environment in the St. Lawrence Seaway is significantly different from that in Prince William Sound and Valdez, Alaska for which a previous version of SPES was developed. The Seaway consists of long and narrow channels punctuated by locks with small clearances under the keel. The tolerances are tight and the room for error is very little. Further, the variety of ships that transit the Seaway is higher and the crews are multinational with limited familiarity with the Seaway, and often, with the English language.

The PC-based SPES is intended to support the functional requirements of piloting ships through the St. Lawrence Seaway, as well as command and control decision making, for different types of users transiting the Seaway. The software architecture implemented provides situation awareness, situation assessment, situation control and scenario display capabilities, and also embeds the types of knowledge required to support the above functional requirements.

In Phase 1, fundamental piloting and command and control decision making are supported. In Phase 2, more advanced piloting, command and control decision making will be supported, and the system will also be interfaced with on-board electronic and navigational equipment such as an Electronic Chart Display and Information System (ECDIS).

The Phase 1 development effort covered a period of one year, from September 1994 to August 1995. The Phase 2 effort is planned over the period of September 1995 to August 1996. Some of the issues that need to be considered in future efforts include seamless integration of tools used to develop PC-based SPES, development of new inferencing rules to reflect the different navigational environment in the St. Lawrence Seaway, and cooperative distributed information sharing between the ship-and-shore based SPES.

# PROTOTYPE PC-BASED SHIPBOARD PILOTING EXPERT SYSTEM FINAL REPORT

## 1.0 INTRODUCTION

Significant changes in the size and complexity of ships coupled with simultaneous crew reductions have made the demanding task of piloting these vessels in congested waterways more stressful (Grabowski & Wallace, 1993). The bridge crew is required to make real-time decisions, and at the same time, avoid information overload. Decision aid technology, incorporating the expertise of the pilot and the bridge crew, has been utilized to assist in the task of piloting so as to result in improved decision making.

In 1986, Rensselaer Polytechnic Institute (RPI) began developing a demonstration prototype system to provide decision support for ships' pilots and officers on watch aboard large vessels in congested waters. The project, developed for the piloting area of New York harbor, demonstrated that a piloting expert system could assist the shipboard navigation officer as well as the pilot.

Following the 1989 *Exxon Valdez* grounding, RPI began the development of an embedded intelligent piloting system, the Shipboard Piloting Expert System for Prince William Sound and Valdez, Alaska. The SPES was developed as an embedded software system within the Sperry Marine Inc. Exxbridge integrated bridge system developed for Exxon Shipping Company tankers (Denham, 1993) in the Trans Alaskan Pipeline System (TAPS) trade (Grabowski & Sanborn, 1992; 1995). The SPES was developed on a Sun workstation/Unix platform using KEE (the Knowledge Engineering Environment), a specialized expert system shell (Fikes & Kehler, 1985).

The purpose of the current project, which follows this earlier work, is to develop a prototype PC-based version of the Shipboard Piloting Expert System and develop SPES modules for a new piloting area - the St. Lawrence Seaway. The operating system chosen is Windows-NT, which runs independent of DOS and its inherent limitations, and the primary programming language is C++, which offers an object oriented software development environment needed to support the knowledge representation scheme used in SPES.

The prototype PC-based SPES will be developed in phases, with increased functionality provided in each phase of development. Phase 1 development, which was funded by the U.S. Coast Guard's OPA-90 Research Grant DTRS-57-94-G-00077, and is the current effort, occurred between September 1994 and August 1995. Fig. 1 shows the Phase 1 development tasks. Follow on work required (i.e., Phases 2 and beyond) is discussed in section 10.

This document outlines the functional requirements of the Phase 1 prototype PC-based Shipboard Piloting Expert System (SPES), provides a description of the current prototype, and provides a discussion of future work.

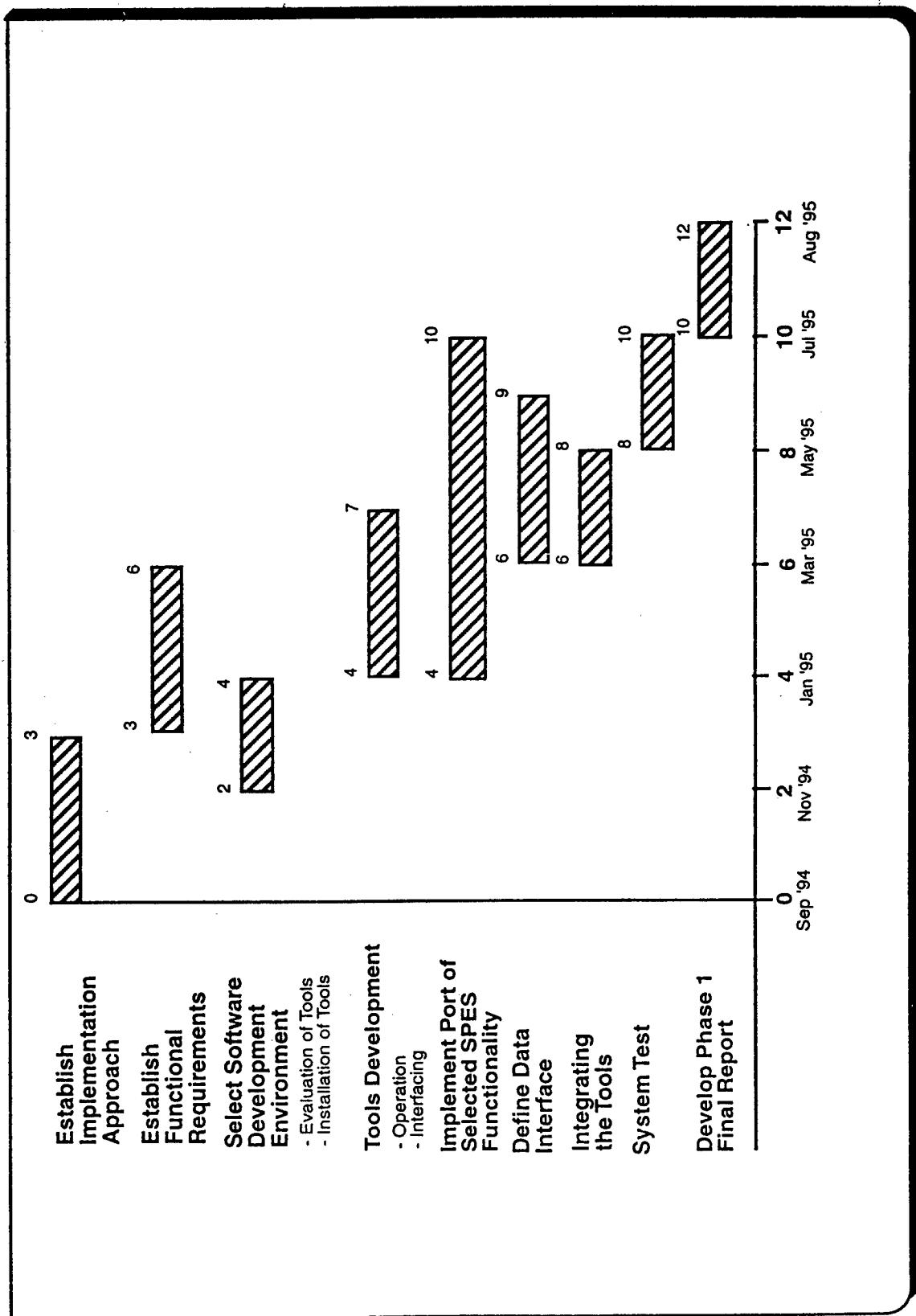


Figure 1. Work Plan for PC-based SPES -- Phase 1

The conceptual design and the functional architecture of the Valdez SPES are retained in the PC-based SPES. However, the functional requirements for the PC-based SPES reflect piloting requirements for the St. Lawrence Seaway. The Phase 1 PC-based SPES represents piloting knowledge between the Eisenhower lock at Massena, NY and the Iroquois lock at Iroquois, Ontario, Canada, and incorporates electronic chart display of the Seaway between the Eisenhower and Snell locks using the Transview system developed by the Volpe National Transportation Systems Center using Canadian Hydrographic Service (CHS) charts. The PC-based SPES will be demonstrated in standalone mode during Phase 1.

## 2.0 FUNCTIONAL REQUIREMENTS

The objective of the PC-based SPES project is to develop and demonstrate an operational piloting expert system on a PC/Windows platform which will provide decision support to the ships' navigation officers while piloting large vessels in a restricted and controlled environment. Following the functionality of the Valdez SPES, the PC-based SPES provides on-line course, speed, position and voyage plan recommendations during the transit. This is provided to assist the bridge team in the activities of trackkeeping, maneuvering and collision avoidance, as well as in the practice of good seamanship, all of which are the essence of good piloting (Grabowski & Wallace, 1993).

Piloting large vessels, while largely a visually dependent activity, also requires expert knowledge. The visually acquired information such as navigational aids or landmarks sighted needs to be processed and interpreted and acted upon. In doing this, pilots use the three types of knowledge - local knowledge, transit-specific knowledge and knowledge of shiphandling (Grabowski & Wallace, 1993) - that they have acquired by study of charts and publications of the navigational area as well as by practice and experience. The PC-based SPES is intended to reduce information overload for the ships' navigation officers and pilots by utilizing encoded local, transit-specific and shiphandling knowledge, to assist them in the task of piloting and navigation.

The knowledge that is embedded in the PC-based SPES is derived from three sources: *piloting functional requirements*, or knowledge that is required to support the tasks of trackkeeping, maneuvering and collision avoidance, and the practice of good seamanship on the Seaway, and reasoning about those tasks; *command and control decision making requirements*, or knowledge required to support situation awareness, situation monitoring, system control and scenario display capabilities; and *integrative functional requirements*, or knowledge required to integrate piloting and command control decision making reasoning.

Piloting functional requirements are derived from piloting heuristics used by Seaway pilots in navigating vessels through the water; command and control decision making functional requirements are derived from shipboard operational, navigational, shipping company organizational, environmental and regulatory requirements for vessels on the Seaway. Integrative functional requirements are derived from requirements to interface and interlace piloting and command and control decision making reasoning in a coherent fashion.



For the St. Lawrence Seaway, *piloting* involves navigating the ship through long, restricted channels with small under keel clearances. To assist the pilot and bridge team in this activity, the PC-based SPES provides them with the current position of the ownship within the navigable channel of the Seaway and alerts them to potential threats of collision or grounding. The SPES also recommends appropriate actions to mitigate the threats, and provides an assist and reminder capability throughout the transit.

The physical, environmental and operational features of the St. Lawrence Seaway result in operational functional requirements. For example, in the narrowest part of the Seaway, the channel width is about 400 feet and the depth of water is only 27 feet. The locks are 80 feet wide, restricting the beam of vessels transiting to 78 feet. In contrast, for the Valdez SPES, the minimum channel width is 2700 feet (at Valdez narrows) and the average water depth in Prince William Sound is 900 feet. In addition, two way traffic is allowed in a single channel on the Seaway, in contrast to one-way traffic inside a Traffic Separation Scheme over much of the Prince William Sound.

Flow conditions in the Seaway significantly impact the transit by influencing phenomena like currents, bank suction and the like. In many navigational situations, vessels on the Seaway pass close by each other, with tolerances of less than 100 feet; the effects of currents, bank suction and vessel bow waves are thus important in vessel navigation. Pilots often determine preferred meeting places throughout the transit, and navigate to those places.

On the St. Lawrence Seaway, vessels are of two types: lakes vessels, which transit the St. Lawrence Seaway almost exclusively, and oceangoing vessels (known as "salties"), who transit the St. Lawrence Seaway and the Great Lakes bringing cargo from other ports. In the former case, lakes vessels are familiar patrons of the Seaway, and the vessel masters and crews speak English; ship's officers may, in fact, have pilotage for the Seaway and the Great Lakes. These are one set of users for the PC-based SPES.

In contrast, oceangoing vessels may make one or more trips through the Seaway in a year, oftentimes have multinational crews with limited facility with the English language, and have limited familiarity with the Seaway and its physical, environmental, operational, and regulatory requirements. These are another set of users for the PC-based SPES. The requirements for the Seaway pilots, the third set of users of the PC-based SPES, are different, depending on whether the vessel is a saltie or a laker. For lakers, pilots take the conn and might use the PC-based SPES as a reminder and assist aid, since pilots are able to confer and converse the bridge watch teams and vessel masters. In addition, pilots are probably more familiar with the bridge electronic and navigational equipment installed aboard the lakes vessels they pilot frequently.

On the other hand, on oceangoing vessels, pilots might use the PC-based SPES as a cross check for basic navigational information and might refer to the system more often, as interface and conference with bridge teams and vessel masters might be limited, and the pilot may be less familiar with the electronic and navigational equipment installed aboard less frequently seen and piloted vessels.

The presence of locks adds another factor to the task of navigating the Seaway. Tolerances in dimensions such as beam, length and draft as well room for maneuvering are tight throughout the Seaway, especially so in case of the locks. Further, the availability of the relevant lock during any point in the transit may affect the voyage plan of the ship and in turn, the actions of the navigation officers of the ship.

Thus, different operating conditions and the nature of threats posed need to be handled by the additional reasoning and functionality developed for the Seaway. For example, the physical dimensions of the ownship are particularly important on the Seaway because navigation tolerances are tight. In assessing the threat of grounding in the narrower and shallower sections of the Seaway, all available navigation options - such as the availability of sufficient areas of deep water *outside* the navigable channel - need to be taken into account in order to develop recommendations to mitigate the threat of collision.

Support for *command and control decision making* is derived from several decision making models. Decision making is often modeled as a process of evaluating and choosing from a set of alternative courses of action, often, in a high-risk, stressful, time-constrained environment. Support of command and control decision making requires an assessment of the current situation, a constant monitoring of the current situation, control of the situation to mitigate the threats assessed by the situation assessment, and display of the current scenario and the recommendations developed to the operator responsible for the decision making.

Functionally, the PC-based SPES supports decision making in a safety and time critical environment with situation assessment, system monitoring, system control and display capabilities. The situation assessment capabilities determine the current status of ownship, assess the impact of existing and new information from the knowledge base as well as the from external systems, and evaluate the targets and threats posed. The system monitoring capabilities monitor and update current situation by interfacing with on-board real-time systems (or the scenario file, in the off-line mode). The system control capabilities coordinate the execution of the system. Display capabilities provide the user with graphic, text and aural (if required) output.

The decision support provided by the SPES should be both timely and accurate, especially because of the close tolerances prevailing in the Seaway. This requires that the PC-based SPES provide response in real-time. Given the operating conditions on the Seaway, an assessment of the current situation of ownship and the surrounding Seaway environment, the length of time required for the vessel to travel a shiplength can be considered as an adequate response. Based on the existing speed restrictions in the Seaway, as well as the size of the ships that can transit the Seaway, this translates into a response time of about 30-40 seconds per assessment cycle. The response time also would include incorporating feedback from the navigation officers as well as on-board systems such as an Electronic Chart Display and Information System (ECDIS).

Supporting the above functionality as well ensuring adequate response time implies access to reliable and timely data, such as ownship speed, heading, location, locations of other vessels

and radar targets, heading and speed of those radar targets, ambient conditions, current and flow conditions in the river. This necessitates a real-time interface between the PC-based SPES and the on-board systems installed. Further, to support the close tolerances prevailing in the Seaway, the data available to SPES - especially location data - needs to be extremely accurate and reliable, such as locational data from at least one Differential Global Positioning System (DGPS) receiver on board, for example.

In Phase 1, fundamental piloting, command and control decision making, and integrative requirements are supported. In Phase 2, more advanced piloting, command and control decision making and integrative requirements will be supported.

### **3.0 ARCHITECTURE**

The system architecture derived from the New York City and Valdez SPES architectures serves as an appropriate framework to conceptualize the PC-based SPES (Fig. 2). The architecture is comprised of four cooperating software modules: Situation Assessment, System Status, System Control and User Interface, which interface with a knowledge base. In addition, an interface definition for an off-line scenario file and an existing Electronic Chart Display and Information System (ECDIS) will be articulated.

#### **3.1 Situation Assessment (SA) module**

The Situation Assessment (SA) module includes routines and algorithms that perform the reasoning involved in collision detection and avoidance as well as grounding detection and avoidance. For collision detection, the SA module accesses the position, bearing, distance, speed, heading of other targets; reasons about the impact of the information on the piloting status of the vessel; and develops recommendations to the bridge crew to avoid the threat. Initially, single ship collision threats will be handled; this will be expanded later to handle multi-ship collisions.

In the case of grounding detection and avoidance, the SA module accesses the position of ownship within the navigable channel and the depth of water, assesses the threat of grounding, and develops recommendations for the threat avoidance.

These assessments and recommendations are stored in the knowledge base for use in future assessments and are also displayed to the user interface as appropriate.

#### **3.2 System Status (SS) module**

The System Status (SS) module handles data input from electronic equipment on the bridge in the case of the real-time mode, or from the scenario file in case of off-line mode. This module receives and reads navigation, radar target, steering, propulsion and other systems data in the form of messages; parses and interprets them; and updates the knowledge base. This

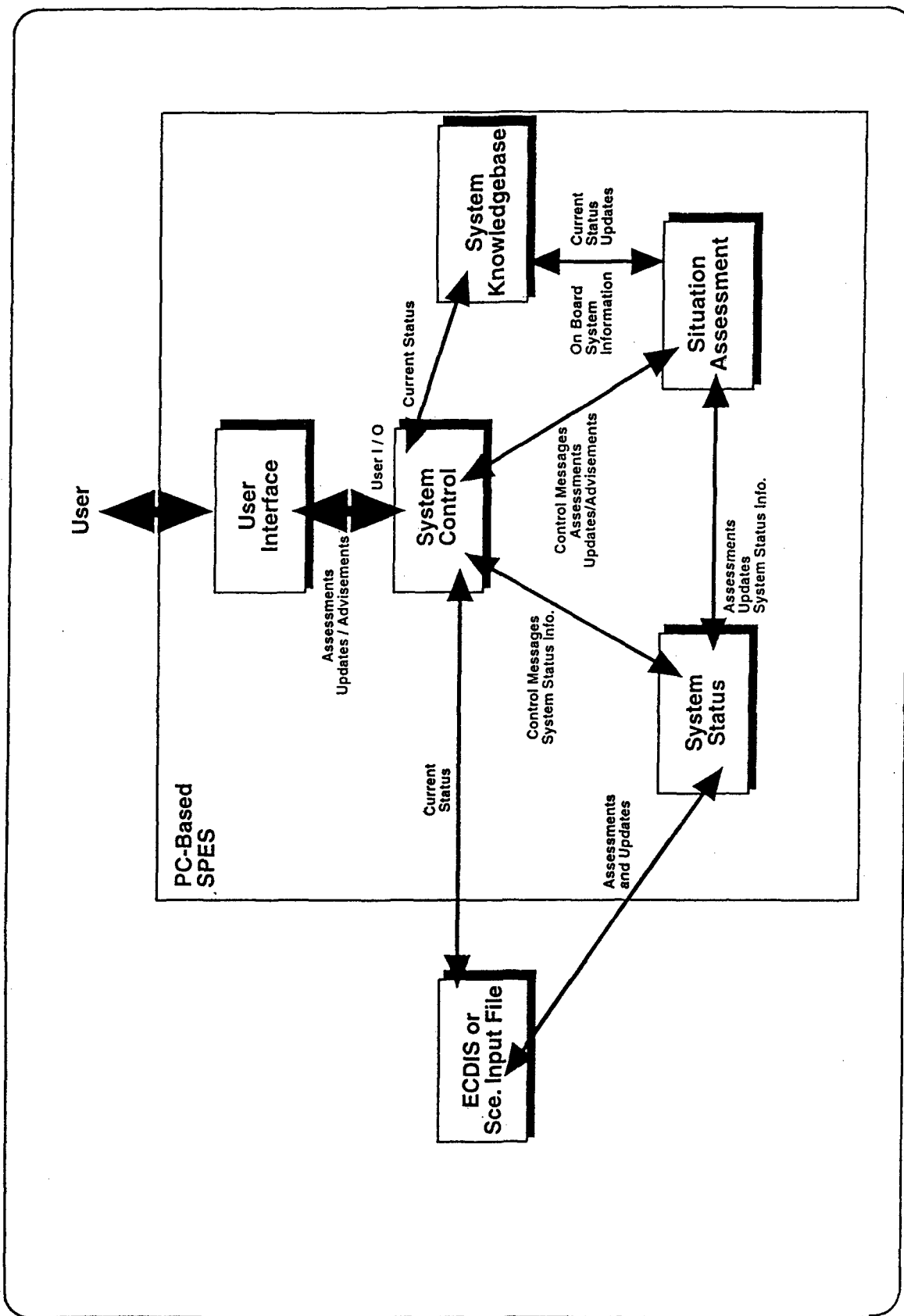


Figure 2: PC-Based SPES Functional Architecture

module may also pass the data on to the SA module for further assessment. System Status input from a scenario file is supported in Phase 1; on-line input is anticipated in Phase 2.

### **3.3 System Control (SC) module**

The System Control (SC) module performs control function for the PC-based SPES. During each execution cycle, this module receives and reads input data, runs the SA module to perform assessment of threats, and generates recommendations. Next, the SC module invokes the User Interface to either display the results using SPES windows or passes them on to a chart system for a graphic display. Thus, the SC module drives the execution of SPES.

### **3.4 User Interface (UI) module**

The User Interface (UI) module formats the SPES output, both text and graphic, and displays the output. Text output is displayed within SPES windows. This includes SPES-generated alerts, advisements, as well the 'remind and assist' messages.

In Phase 1, the Transview System electronic chart will be used to provide the system's graphic output; SPES overlays and underlays to the Transview systems will be displayed so as to simulate an integrated text and graphics display. In future phases, SPES text and graphics output will be displayed as over- or underlays to an existing electronic chart display and information system (ECDIS).

### **3.5 System Knowledge Base (SKB)**

The System Knowledge Base (SKB) provides objects and data for current situation assessments, including transit-specific information, chart object information, and the alerts and advisories in effect currently (Grabowski & Sanborn, 1992). The SKB consists of the rule base developed in the SPES reasoning tool and the knowledge base developed using C++ object system and C++ taxonomy.

## **4.0 HARDWARE ENVIRONMENT**

The Phase 1 PC-based SPES has been developed on a Zenith Pentium 90 MHz Z-station EX with 16 MB RAM, 540 MB harddisk, one 3 1/2" floppy drive, one CD-ROM, 2 serial and 1 parallel ports. In addition, a SVGA video adapter with 1280x1024 resolution and a video accelerator board with 2MB RAM, as well as a 15" color monitor, keyboard and mouse provide the hardware platform for the Phase 1 development effort.

## 5.0 SOFTWARE ENVIRONMENT

The software environment for the PC-based SPES was selected to provide object oriented knowledge representation and rule-based inference capabilities on a PC platform using commercial off the shelf software (COTS). Towards this end, the Phase 1 PC-based SPES software environment includes:

- 1. The Microsoft Windows-NT Version 3.5 Operating System,
- 2. Microsoft Visual C++ Version 2.0 program language,
- 3. A reasoning tool to provide for rule-based inference capability using the C++ object scheme. The reasoning tool also provides the taxonomy to develop the knowledge base using C++ object system.
- 4. The Transview Chart System developed by David Phinney of the Volpe National Transportation Systems Center, which provides the electronic chart display for the PC-based SPES.

## 6.0 INTERFACE CONCEPT

In Phase 1, the PC-based SPES will be interfaced with the Volpe Center's Transview system which provides the electronic chart base for the system. The Phase 1 PC-based SPES interfaces with the Transview chart system by running Transview as a separate process and periodically updating Transview to display the graphic output. The interface specifications are being refined in consultation with the developers of Transview.

In Phase 2, the PC-based SPES be interfaced with an existing ECDIS. The interface will provide for input of radar target and tracking information as well as data from ownship systems. This input will be used with the knowledge in the knowledge base for reasoning in the Situation Assessment module and arriving at alerts, advisements and recommendations to the user.

### 6.1 Phase 1 Interface Concept

In the Phase 1 prototype, the transit of a vessel between the Eishenhower lock and the Iroquois lock is simulated using scenario files. The location of the various navigational aids and the location of line segments that form the edges of the navigable channel are loaded from data files to construct the chart-objects knowledgebase. The input from a simulated on-line bridge system is read periodically and this input drives the simulation. The transit plan is developed so as to keep the ownship in the middle of the navigable channel.

In the Phase 1 prototype, only the threat of grounding is considered. At each ship position, the distance of the ship from the edge of the channel segment is calculated and the depth of water is considered. Any deviation from the expected and safe position will result in an alert message.

Each inference cycle begins with reading a frame of data from the scenario file. Each frame includes data on the position of ownship, depth of water and the location of all the radar objects tracked. The Situation Assessment routines verify whether the ownship position is within the navigable channel. If not, an alert will be raised within the SPES window and the User Interface routines will invoke Transview to show the ownship position.

If the vessel is within the navigable channel, the distance to the nearest point on the channel edges is calculated. This information, along with the position of ownship and the depth of water are passed on to Transview for display. In addition, the location of all radar targets within an alert radius (currently set at 1 mile, but variable) are also passed on to Transview. Figure 3 shows the PC-based SPES screen utilizing Transview charts, showing the position of ownship and the relevant section of the Seaway.

Thus, at each execution cycle, the ownship position, the alert radius circle, the layout of the navigable channel and the position of any radar targets which are within the alert radius are transmitted to Transview in the form of map overlays for display. Also, a message is sent to Transview to update the Transview. SPES waits for conformation of the display update from Transview before continuing execution.

The alert messages display if ownship is outside the navigable channel or if ownship is too close to the edge. Routine reminder messages, such as any applicable required radio contacts at each point are also displayed using SPES windows. Figure 5 given an example of the PC-based SPES screen with a warning to a vessel too close to the channel edge.

## **6.2 Phase 2 Interface Concept**

The Phase 2 interface consists of real-time input from ownship systems including radar, navigation electronic equipment and electronic chart display and information systems (ECDIS). In Phase 2, the ECDIS will provide to the PC-based SPES target and tracking information, including track file histories.

This information will be used by the Situation Assessment module to determine the nature of the threat posed by different acquired targets and to determine the recommendations developed by the PC-based SPES, based on the threats posed.

Input from ownship systems will be provided to the PC-based SPES in the form of heading, speed, course to steer, course steered, course made good, propulsion plant information, weather and current data, navigation and steering systems input, as well as input and flags provided by the vessel management systems of the vessel. The integrated bridge system messages containing ownship information are acquired via an interface unit, interpreted in the System Control module and forwarded to the System Status module.

## 7. OPERATIONAL EXAMPLE

In order to put the PC-based SPES in context, consider the following scenario. On the St. Lawrence Seaway, the task of the pilot and master is to safely navigate the Seaway while dealing with real-time problems and unusual circumstances as they arise. A typical Seaway transit consists of the vessel passing through a sequence of transit legs often punctuated by transit between two locks. The Phase 1 PC-based SPES shows an example of a transit between the Eisenhower lock and the Iroquois lock, representative of the sequence of transit legs that comprise a complete passage of the Seaway.

In this example, the transit of a ship of length 500 feet, with a beam of 70 feet and a draft of 24 feet is considered. Figure 3 depicts the navigational situation display we would expect the PC-based SPES to offer to the bridge team as the ownship is leaving the Eisenhower lock. The information displayed includes:

- threat of grounding indicated by the distance of the ownship from the edges of the navigable channel,
- threat of grounding indicated by the depth of the water below the keel of the ship. Given the close tolerances of depth in some segments of the Seaway, any deviation from expected depths should be a matter of concern to the bridge crew,
- an alert circle which marks the region of interest around the ownship within a given radius ( 1 mile in the example),
- threat of collision represented by the presence of radar targets, especially those targets within the alert radius (not shown).
- the current course and speed of ownship.

In addition, any local information of interest to the bridge team is also displayed such as wind conditions, current location of ownship in terms of known landmarks (Eisenhower lock in Figure 3) and the like. The plan view of the ship along with the relevant segment of the Seaway is depicted in the Transview window, and the text information is shown in the "SPES Information" window.

Figures 4, 5, 6 and 7 depict the progress of ownship through the Seaway and the corresponding SPES displays. The section of the Seaway between the set of red buoys and green buoys is defined to be the navigable channel and the navigable channel is overlaid on the Transview charts.



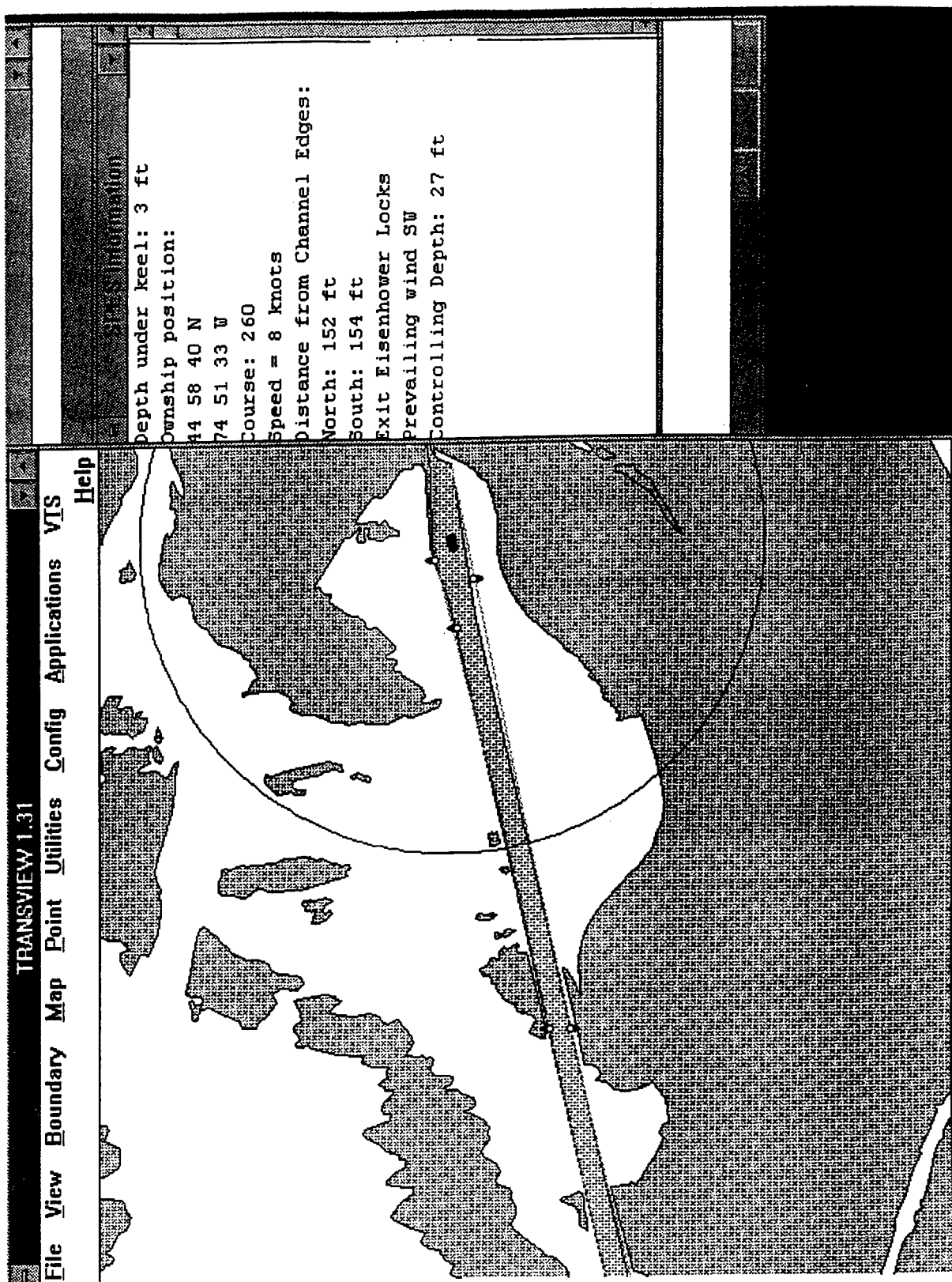


Figure 3. Operational Example

Figure 4 shows the ownship entering a section of the Wiley-Dondero canal of the Seaway which is an one-way zone and this information is provided to the pilot and master. As earlier, the progress of the ownship is shown not only in terms of the latitude and longitude but also in terms of known landmarks and navigational aids (buoy 44 in this case).

Figure 5 shows the ownship further upstream and also shows the warning generated whenever the ownship comes too close (within a predefined distance) to the edges of the navigable channel. A beep will sound, alerting the bridge crew to the potential threat of grounding and the warning message is displayed in the SPES Information window.

The 'remind and assist' capability of the PC-based SPES is shown in figure 6. The ownship is passing a VTS call-in point (VTS call-in point number 11) and a reminder is generated along with the suggested actions to be undertaken. The speed restriction that is applicable in the relevant section of the Seaway is also displayed. Alerts are also generated if ownship exceeds the speed limit in effect.

In figure 7, the ownship is passing through a region where there is a strong bank suction present (near Mariatown range, close to the Iroquois lock). The SPES Information window displays a cautionary note about this local information. The example ends when the ownship reaches the Iroquois lock (not shown).

## **8. PHASE 1 DESIGN AND DEVELOPMENT**

This section describes the work completed on Phase 1 of the PC-based SPES project. The goal for Phase 1 of the PC-based SPES development effort was to demonstrate the feasibility of implementing the SPES on a PC platform in the off-line mode, driven by a scenario file, for a new piloting area, the St. Lawrence Seaway. This development involved exploration of 3 major issues:

1. Porting of the object-oriented data and knowledge structure as it existed in the Valdez LISP/KEE implementation of SPES into C++. The software created in the St. Lawrence Seaway PC-based SPES takes into account the differences between the two software environments and is sufficiently robust to support the required processing.
2. Development and integration of a chart system to display results. In Phase 1, an existing chart display system, the Transview system, is utilized. The multiprocessing capability of Windows NT greatly facilitates such an approach. Though the Transview and the PC-based SPES are PC-based, using C++ and Windows, the differences between the 32-bit Win32 API environment (of SPES) and the 16-bit Win16 environment (of Transview) pose some problems in ensuring a seamless integration. However, the potential migration of Transview to the emerging Win32 API environment will obviate this bottleneck.

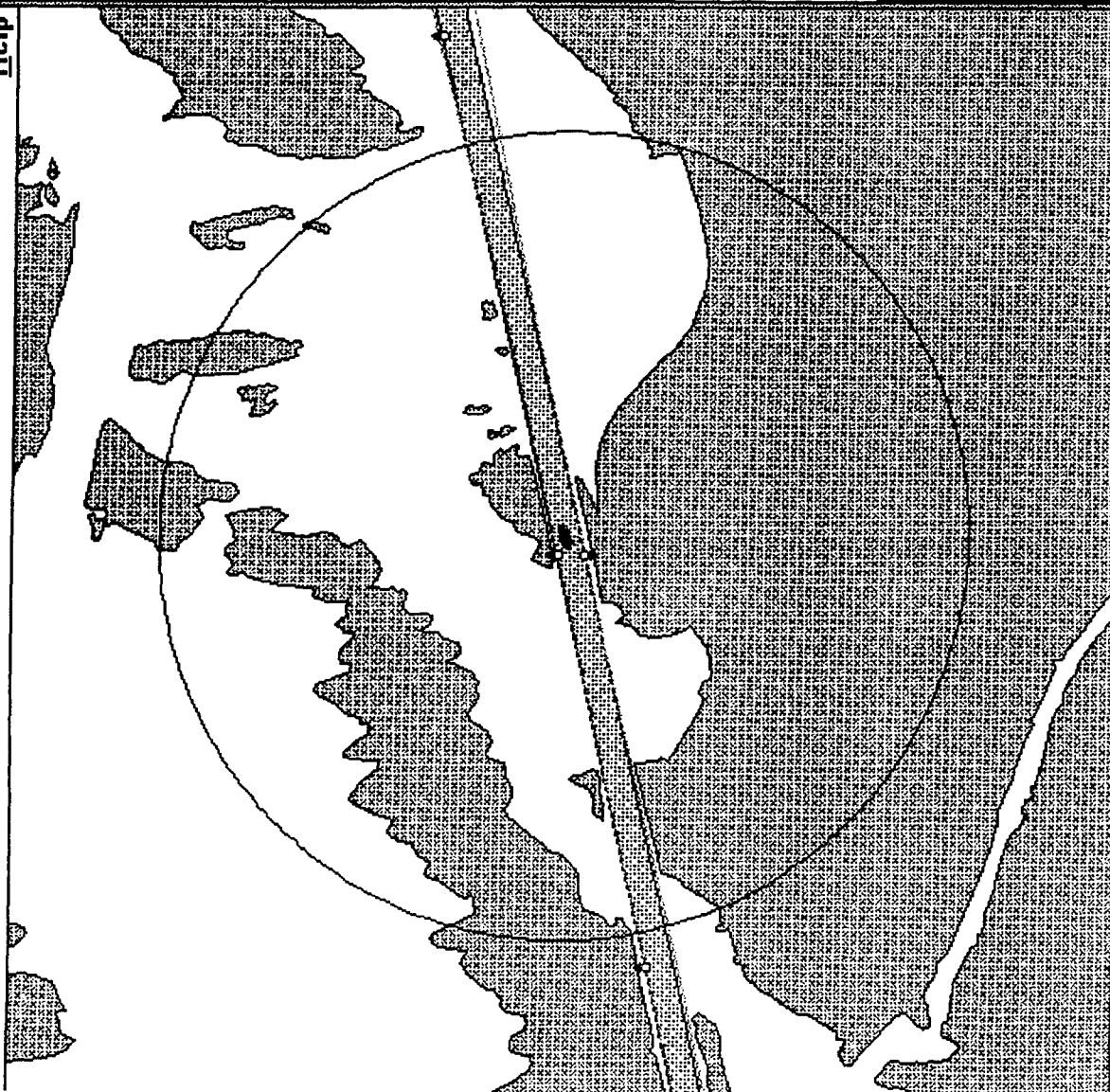


Figure 4. Operational Example

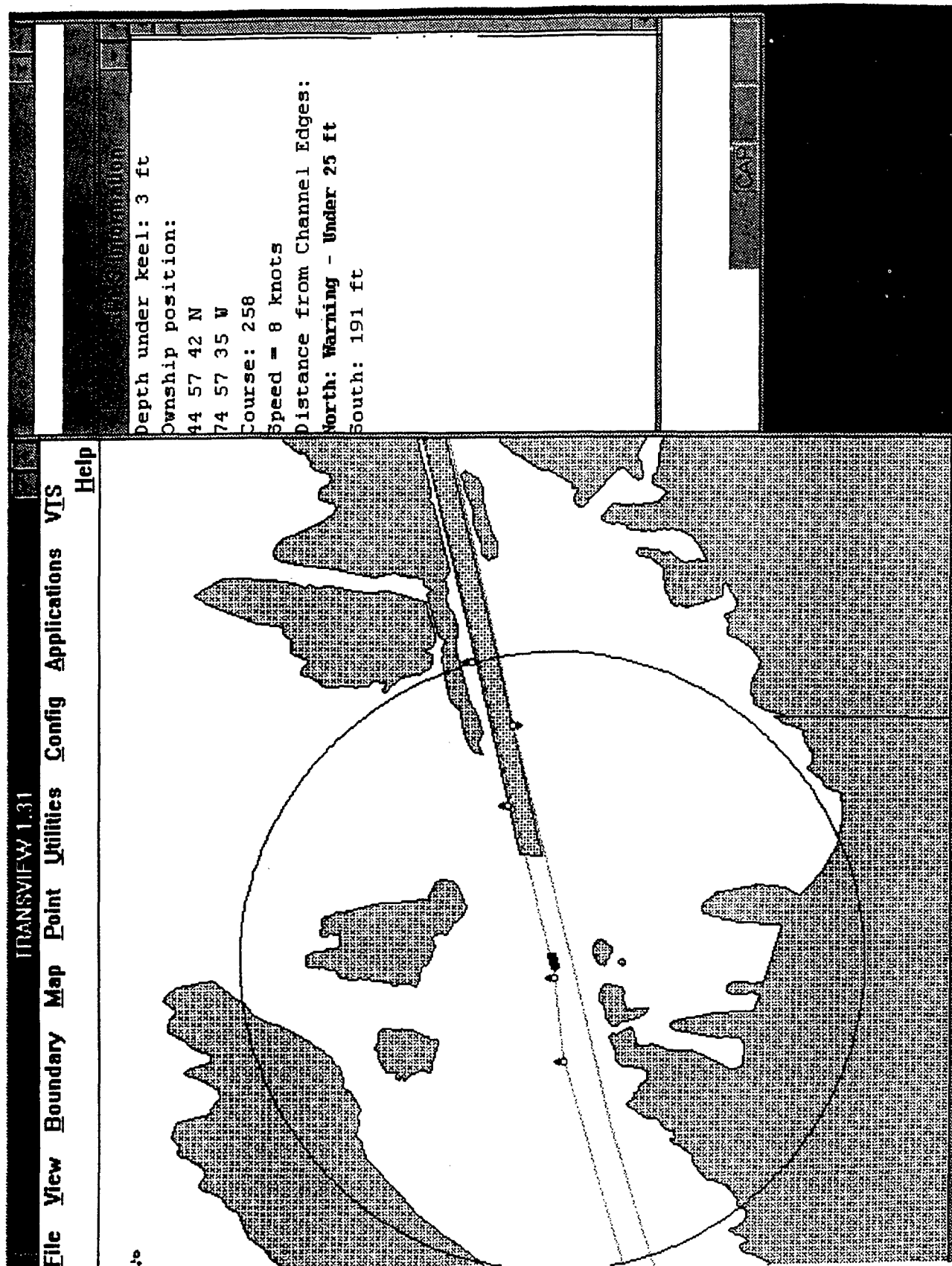


Figure 5. Operational Example



## SPES Information

Depth under keel: 15 ft  
Ownship position:  
44 55 38 N  
75 5 15 W  
Course: 261  
Speed = 8 knots  
Distance from Channel Edges:  
North: 509 ft  
South: 289 ft  
Speed Restriction: 13 knots  
VTS Call-in Point #11  
Call Seaway Eisenhower  
and Seaway Iroquois: Give  
Vessel Name, Speed, Course, ETA

Figure 6. Operational Example

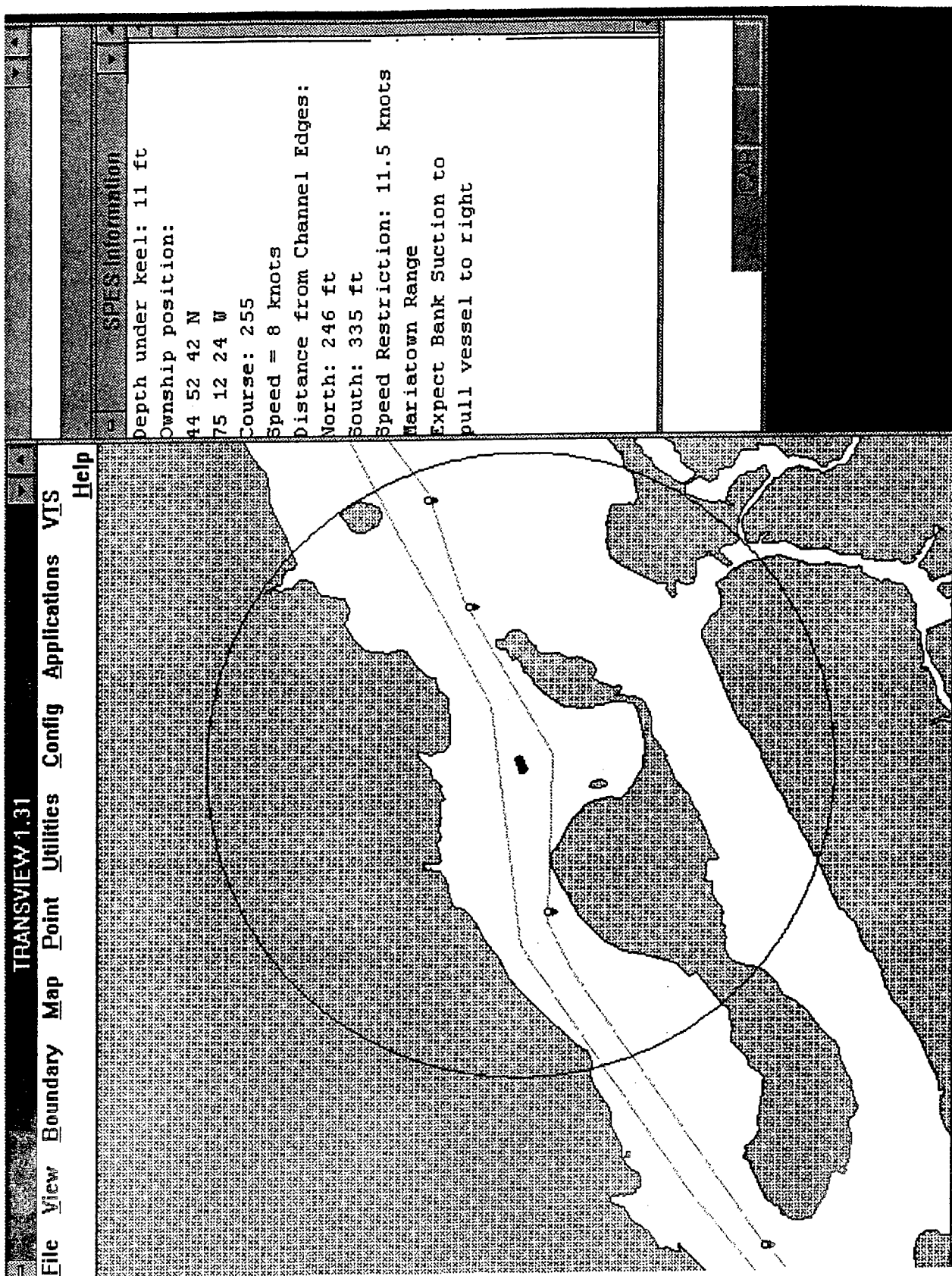


Figure 7. Operational Example

3. Developing a knowledge representation approach for inferencing using production rules and backward chaining, which also supports object oriented representation of the domain knowledge. To facilitate the development of a suitable knowledge representation so as to enable the coding of production rules as well backward chaining mechanism for inferencing in SPES, a reasoning tool is utilized which provides the required functions as well as works with C++ objects.

## 9. COMPARISON OF PC-BASED SPES TO ITS PREDECESSORS

The PC-based SPES is the third product to have evolved from the Piloting Expert System concept (the New York City Piloting Expert System - PES, and the Valdez Shipboard Piloting Expert System - SPES, being the other two). As such, it exhibits several differences from previous versions:

- The PC-based SPES prototype is the first step in the *migration* of SPES from a specialized software development environment to a general software development environment, using off the shelf tools and components.
- Several separate software and hardware components are used to implement the PC-based SPES. For example, one software tool has been chosen to implement the chart display, and another used to implement the knowledgebase. Given the different software and hardware components, *integration* of these components to produce the required functionality is a critical issue and involved considerable time and effort - both in terms of programming and interacting with outside developers and support personnel. Thus, integration challenges were at least as demanding as development of the software.
- The piloting area (domain) for the PC-based SPES is also very different. The St. Lawrence Seaway is extensive (165 miles from Montreal to Lake Ontario and 2342 miles from the Atlantic Ocean to Duluth, Minnesota) - incorporating controlled, narrow and shallow segments, gateways (locks) as well as relatively open waters segments. The transit length is much longer and the tolerances in terms of the physical dimensions as well as room for maneuvering are much tighter. The river bottom is also rather unforgiving. These factors, as well as the small depths under the keel, result in little room for error.
- The variety of ships transiting the Seaway is also greater, in contrast to the single ship type (oil tankers) considered in the Valdez SPES. For example, the vessels include bulk carriers, grain carriers as well as tankers. Further, one can classify the transiting vessels as lakers or salties. The three different types of users were outlined in Section 2. The PC-based SPES needs to be developed to accommodate the variety of vessels transiting the Seaway as well as the three types of users.



- The nature of decision making on the St. Lawrence Seaway is also different. The tighter tolerances and the extremely limited room for errors implies that the decision support must be not only be timely but also very accurate. The response time must be adequate and the response must also incorporate feedback from the user. The variety of vessel crews and their lack of familiarity with the local conditions as well as the English language adds a further twist to the task of providing timely and accurate decision support.

## 10. FUTURE WORK AND ISSUES TO BE CONSIDERED

Phase 1 of the development of PC-based SPES demonstrated the feasibility of porting the SPES from a proprietary platform and specialized tools to a more general platform, using commonly available, general purpose tools. Further development to be undertaken in Phase 2, focuses on extending and refining the PC-based SPES in order to:

- Provide real-time input from on-board systems. This issue must also address the challenge of interfacing with a number of (possibly) incompatible systems installed in the variety of vessels that transit the Seaway. Evolving a common standard for interfacing the PC-based SPES with on-board equipment is an issue that must be considered.
- Enhance the domain knowledge and piloting heuristics in the system, to reflect the operating conditions in the St. Lawrence Seaway. This issue involves providing for the unique operating conditions in the Seaway, covered in earlier sections, as well as addressing the challenge of providing decision support in the prevailing environment.
- Exploit the advantages offered by a more powerful and general purpose platform. The PC and Windows-NT platform is a very powerful hardware and software platform offering a number of features like 32-bit processing and pre-emptive multitasking. The use of Windows-NT makes available a range of software.
- Tackle the issues associated with the integration with an operational ECDIS aboard ship.
- Develop an approach and implementation plan for integration with the PC-based SPES with an operational Vessel Traffic Services (VTS) system.



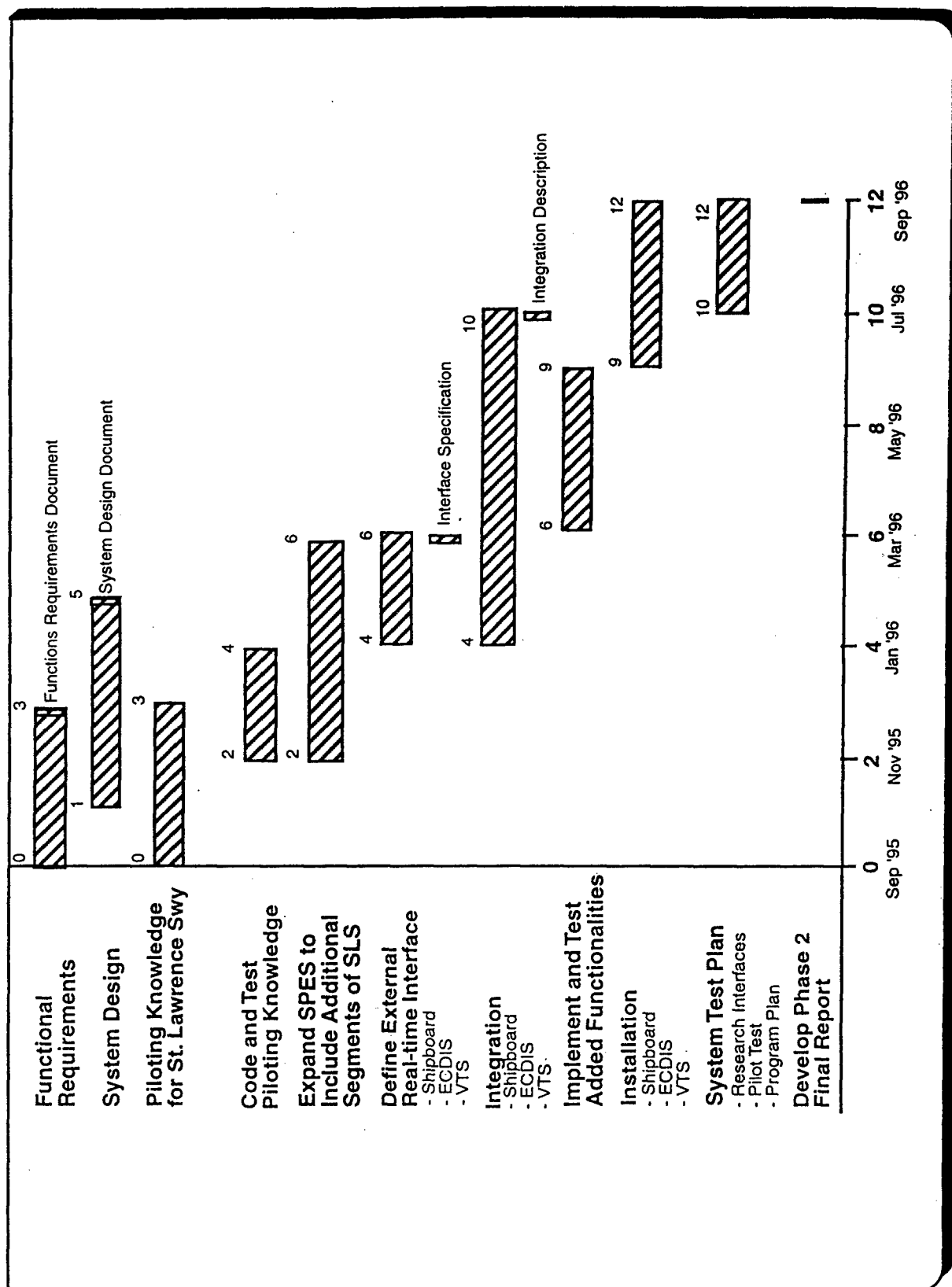


Figure 8. Work Plan for PC-based SPES -- Phase 2

- Develop an approach to measuring the nature and contribution of distributed information sharing in a joint shipboard-VTS-based intelligent piloting system, and
- Develop an understanding of the piloting, decision making, and integrative requirements of distributed, intelligent information systems.

Some of the other issues that need consideration are selection of appropriate tools to exploit the advantages offered by a more powerful and general platform, selection of appropriate knowledge acquisition and knowledge representation techniques for follow-on efforts, incorporating advances in the state of art in both hardware and software, development of interfaces to accommodate the variety of on-board systems on the vessels using the Seaway, and eventually, the development of a common protocol. RPI looks forward to these challenges.

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**DECISION SUPPORT TECHNOLOGY FOR OIL SPILL RESPONSE  
CONFIGURATION PLANNING**

*Roberto DeSimone, SRI International*

## EXECUTIVE SUMMARY

SRI International (SRI) is pleased to present this final report on the tasks undertaken for the Oil Pollution Research Grant Program, which took place between August 1994 and July 1995. Under this research grant, SRI has explored the incorporation of additional artificial intelligence (AI) technology within the existing prototype decision support tool for spill response planning currently under development for the U.S. Coast Guard (USCG) Research and Development Center. As a result, the Spill Response Configuration System (SRCS) now provides more capabilities for addressing resource configuration planning tasks, and also for maintaining the underlying model within the system.

This research relied on the successful transfer of advanced AI technology currently being developed under other Department of Defense (DoD) contracts and also under SRI's Internal Research and Development funds. As a result, we believe that USCG has benefited greatly from access to advanced technology developed under these other contract funds.

This advanced technology includes the incorporation of dynamic replanning techniques into SRCS for modifying response plans based on changes in spill scenarios. These techniques permit the user to explore the consequences of user-specified changes in spill scenarios on response plans and eventual damage to the environment. In this way, the user can explore a much wider variety of resource configuration decisions with greater accuracy and consistency than is practically possible with manual methods. In addition, the SRCS user interface was enhanced to provide more flexibility for refining and updating the knowledge base of the spill response operations and methods.

Demonstrations of the dynamic replanning and enhanced user interface capabilities were given at the International Oil Spill Research and Development Forum, sponsored partly by USCG, and held at the International Maritime Organization Headquarters in London, England, at the end of May 1995, and also at the USCG Oil Pollution Research Grant Presentations held at Volpe National Transportation Systems Center (VNTSC) in Cambridge, Massachusetts, during 9-10 August 1995.

As a result of development and demonstrations under this grant and others, SRCS is ready for field testing and application. The range of contingency planning needs that the USCG faces under the Oil Pollution Control Act of 1990 (OPA 90) mandate, at the national, regional, and area levels can be improved by application of this tool to determine adequacy of equipment in terms of shortfalls and siting locations. With further development, this technology for planning and evaluation can be applied to meet a range of USCG planning needs. To summarize, the range of tasks to which it applies includes

- **Contingency Planning.** The development, simulation and evaluation tasks within contingency planning can be improved in accuracy and speed with the current SRCS.
- **Training.** Users of the tool can benefit from the knowledge about planning that has been incorporated in SRCS. By developing better user guidance and explanation capabilities, the system could be developed into a training tool for USCG officers and contractors.
- **Spill Response Planning and Execution.** During a spill incident, SRCS gives the ability to undertake activities with foresight, rather than in response to the immediate crisis. The replanning and execution abilities of the automated planning technology can modify a plan to track an evolving situation, so that the plan is current with the best information available at the time. This capability would require incorporating the SRCS technology within a command and control system for oil spill response.

# 1 INTRODUCTION

SRI International (SRI) is pleased to present this final report on the tasks undertaken for the Oil Pollution Research Grant Program, which took place between August 1994 and July 1995. Under this research grant, SRI has explored the incorporation of additional artificial intelligence (AI) technology into the prototype decision support tool for spill response planning that is currently under development for the U.S. Coast Guard (USCG) Research and Development Center. As a result, the Spill Response Configuration System (SRCS) now provides more capabilities for addressing resource configuration planning tasks, and also for maintaining the underlying model within the system.

## 1.1 INTRODUCTION

Since the introduction of the Oil Pollution Act of 1990 (OPA 90), there has been a considerable increase in the amount of time and effort spent in developing and revising oil spill response contingency plans. The USCG is responsible for ensuring that regional and district spill contingency plans are revised and updated regularly (normally every 2 years). Such contingency planning activities are undertaken within the area committees for each of the USCG regions and districts, with the USCG as chair of the committees.

As the required number of contingency plans multiplies, due partly to the increasing number of sensitive areas, the process of generating, analyzing, validating and verifying these plans becomes more time consuming and prone to error. If decision-support technology were used more extensively, more contingency plans could be generated and evaluated, and a more consistent framework could be developed for generating and evaluating such plans for the entire U.S. coastline. The general use of such technology would also minimize the number of errors introduced into either the response plans or the results derived from them. Furthermore, the costs of entering new information into databases and knowledge bases would be significantly outweighed by the benefits derived from more frequent updates to contingency plans, which would be more accurate and easier to convert and tailor for specific spills.

The research performed under this grant has added capabilities to the existing prototype of the decision support tool, SRCS, that had been developed between February 1993 and August 1994. The SRCS prototype was demonstrated during this 18-month period to USCG personnel from the Marine Safety Offices (MSOs) of San Francisco, Los Angeles, Boston, Providence, New Orleans and New York, and to several USCG staff from the National Strike Force Coordinating Center (NSFCC) in Elizabeth City, from the USCG Commandant's Office of the Marine Environmental Pollution division (G-MEP) in Washington, D.C., and from the USCG Research and Development Center (RDC) in Groton, Connecticut.

Feedback from these demonstrations highlighted the need for additional technology (1) to dynamically revise response plans and resource configurations based on rapidly changing spill scenarios, and (2) to provide a more effective user interface for refining and updating the knowledge base of the spill response operations and methods within SRCS. This research grant has addressed these two topics. Furthermore, it has enabled us to explore how the incorporation of further advanced technology leads to the development of a more visionary spill response planning system that will be suitable not only for spill-response contingency and configuration planning, but also for crisis-response planning and monitoring as well as for command and control activities.

## 1.2 DYNAMIC REPLANNING

It is often the case that as soon as a contingency plan has been developed it is already out of date because of rapidly changing input data, revisions of underlying assumptions or environmental priorities, or the addition of new equipment capabilities. Thus, contingency plans should be flexible enough to deal with a wide variety of spill scenarios. Such flexibility can be achieved by abstracting many of the details within a specific spill response plan so that the plan is more generally applicable to different spill situations. Abstracting the details, however, often makes it difficult to evaluate the consequences of a response plan, since many specific spill response actions have not been identified. Alternatively, one could describe all the possible responses to specific spill situations and include these within the same contingency plan; but such contingency plans tend to be so huge that they are difficult to review and revise. Furthermore, it is unclear whether *all* of the possible responses to spill situations can be explicitly captured in one contingency plan.

Our solution, described in this report, was to extend SRCS with dynamic replanning capabilities that enable the user to explore the consequences of situation changes on the response plan. By representing much more detail within a response plan than is normally recorded in a PERT\* or Gantt chart, such as the objectives and justifications for each of the spill operations and methods, and the dependencies between them, it is possible to develop a response plan that can be easily modified and updated as the situation changes. Instead of static, the plan representation is *dynamic*, in that the structure of the plan changes as the situation changes.

Examples of situation changes include revisions of the spill trajectory caused by factors such as wind direction changes; the unavailability of specific response equipment, such as soiled booms; the effects of weather, such as the disruption of equipment transportation to sensitive areas; and the failure of specific planned actions to achieve their objectives, such as the failure of diversion booming to protect a sensitive area because of heavy seas. SRCS's replanning capability propagates the effects of situation changes throughout the response plan, and determines which parts of the plan are affected by these changes. Alternative actions to compensate for the changes are presented to the user. For instance, if the sea conditions are too rough for a specific type of boom, SRCS identifies the booms that can operate under the current conditions. If no suitable equipment is available, SRCS backtracks to a previous choice and selects an alternative operation that does not rely on booms. SRCS's replanning capability further assists the user by keeping track of the current state of the response plan and determining whether the constraints represented in the current plan are valid. Whenever a change occurs, its effects on the response plan are reported to the user, and revisions to the plan are suggested.

The main benefits of these dynamic replanning capabilities are the following:

- A single dynamic response plan can represent a wide variety of spill response contingencies.
- If the situation changes, it is easy to determine whether the existing plan can be tailored to cope with the change.
- A sensitivity analysis of the response plan can be performed to determine how robust the plan is to situation changes.

The dynamic replanning mechanisms are discussed in more detail later.

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\*PERT: Program evaluation and review technique.

### 1.3 KNOWLEDGE-BASE MAINTENANCE

Successful contingency planning depends on the development of flexible and accurate spill response plans that are appropriate to the *probable* range of spill scenarios for a specific area or coastline. The flexibility and accuracy of response plans is dictated by the completeness and consistency of the underlying spill response knowledge base. If the knowledge base is complete, consistent, and up to date, then one can be confident that the resulting response plans will be appropriate and successful. On the other hand, the task of maintaining a knowledge base is never complete, and new information must be added to the knowledge base periodically. When several people are involved in the process of maintaining and updating a knowledge base, error is always a possibility. One must ensure, therefore, that the new information is formatted correctly and is consistent with the information already entered in the knowledge base. A simple approach would be to enable the user to input textual information directly into the knowledge base. For a user experienced with the knowledge base, this approach may be acceptable; but inexperienced users need more guidance, to ensure that the new information is syntactically and semantically correct. Thus, a structured approach is required for maintaining the knowledge base.

Under this research grant, we explored the incorporation of structured, graphical user interfaces for revising and updating the knowledge base. Such interfaces assist the user in the following tasks: (1) adding new response operations to the knowledge base; (2) revising existing operations by modifying the description of response actions, the applicability conditions under which the operations may be considered suitable, or the types of equipment that may be employed during the operation; and (3) changing the descriptions of the capabilities of the equipment and personnel. Such interfaces permit inexperienced users to change the information in the knowledge base without very detailed knowledge about how the information is represented within the underlying model, thus permitting the knowledge base to be extended and expanded as the new response methods are identified. For instance, the results of recent tests of the effectiveness of response equipment can be incorporated into the knowledge base, so that the environmental damage can be more accurately estimated.

### 1.4 OUTLINE OF REPORT

In Section 2 we provide a brief outline of the current SRCS architecture and descriptions of the underlying technology within some of its modules, in sufficient detail to motivate later discussions of the technology required for dynamic replanning and knowledge-base maintenance.

Section 3 provides detailed descriptions of SRCS's dynamic replanning capabilities, and their application to spill-response planning. Past approaches to replanning are briefly discussed and contrasted with the dynamic replanning techniques. These techniques are described in the context of an example of specific spill response.

Section 4 describes the user-interface capabilities for revising and updating the knowledge base that were added to SRCS under this contract. These new capabilities enable the user to expand and extend the knowledge base as new response methods are developed, or new equipment capabilities are provided by spill response equipment manufacturers.

Section 5 summarizes the main contributions of this project.

Appendix A contains the screen displays from the variant replanning scenario, as demonstrated at the International Maritime Organization (IMO) headquarters in London, UK, and at VNTSC.

Appendix B contains the viewgraphs presented with these demonstrations.



## 2 SPILL RESPONSE PLANNING SYSTEMS

This section provides a brief outline of the current SRCS architecture and descriptions of the underlying technology within some of its modules, in sufficient detail to form a basis for later discussions of the technology required for dynamic replanning and knowledge-base maintenance.

The SRCS architecture, represented by the data-flow diagram in Figure 1, comprises four main modules (shown as oval nodes):

- Equipment and Logistics Planner
- Trajectory Model
- Evaluation Module
- Color Map Display Module.

When developing a contingency plan or exploring a particular equipment configuration, the user must first provide information about the spill to be examined and the equipment available for responding to the spill. This information is represented in Figure 1 by the data-store nodes SCENARIOS and RESOURCES. This information, together with data from the trajectory model denoted as FACTS, constitutes most of the inputs to the equipment and logistics planner. The user can modify the scenario, the locations of spill response resources, or the choices of response

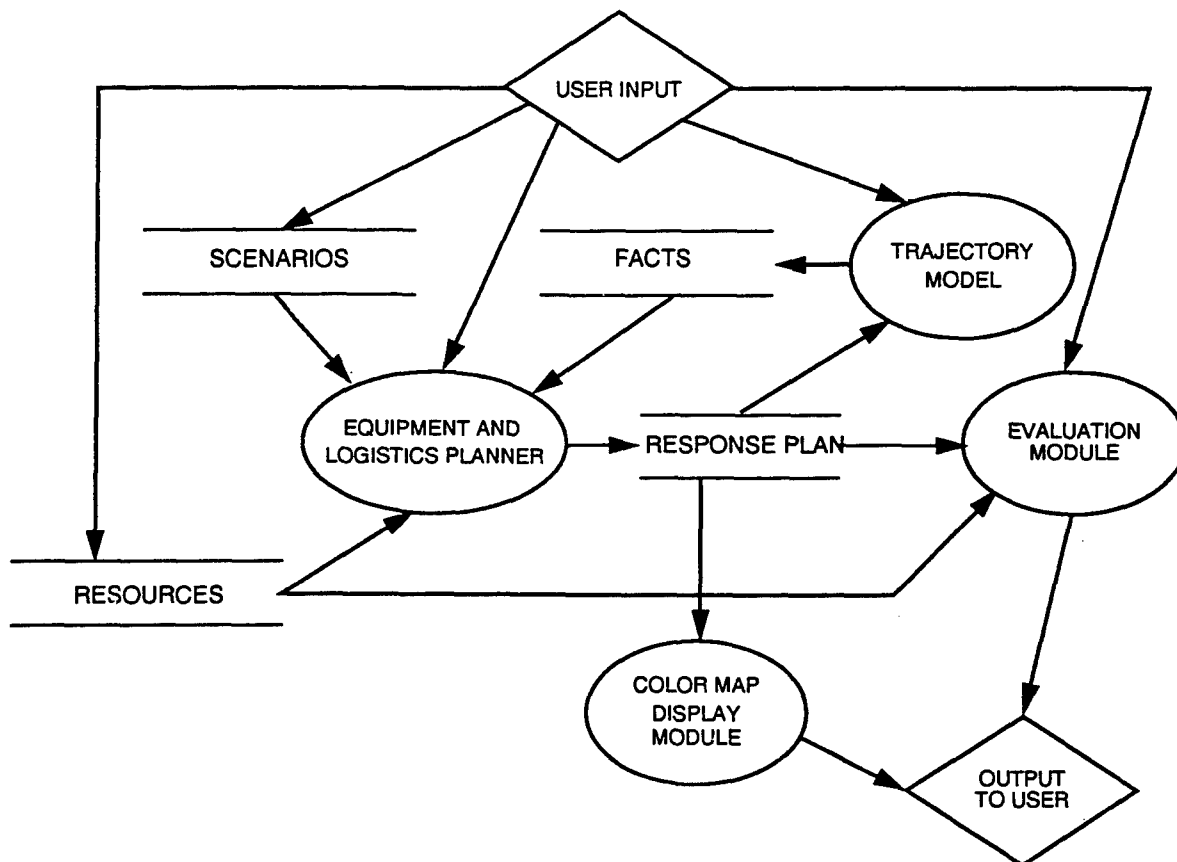
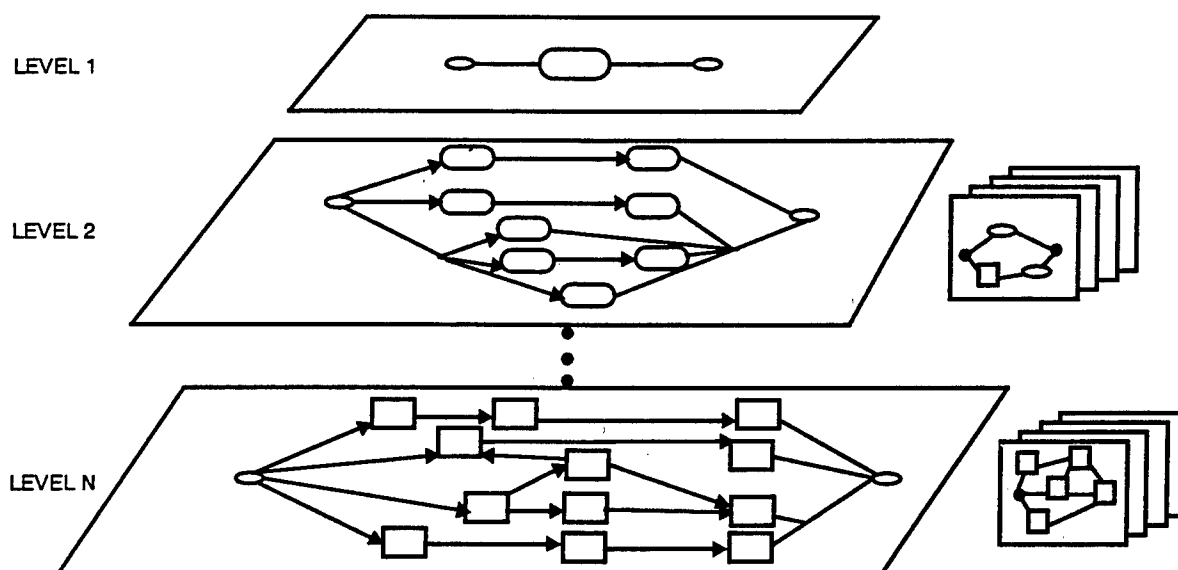


Figure 1. Data-Flow Diagram of SRCS Architecture

operations within the RESPONSE PLAN that is generated. The response plan provides opportunities to update the trajectory model and evaluate the environmental and cost impacts, and presents the plan to the user on a map display.

**Underlying Planning Technology.** The main capabilities of the SRCS Equipment and Logistics Planner are provided by advanced AI planning technology embodied in the System for Interactive Planning and Execution (SIPE-2<sup>\*</sup>). SIPE-2 was developed at SRI during the early 1980s and has been demonstrated on a variety of planning problems. During 1992, it was demonstrated at the Pentagon as a potential military operations crisis action planning tool.<sup>†</sup>

The underlying AI planning technology provides good plan representation capabilities, as well as mechanisms for interactive and automated reasoning. SIPE-2 provides traditional PERT- and Gantt-chart representations of the plans it produces. PERT charts, or partially ordered graphs similar to those shown in Figure 2 provide a standard description of the plan as a set of actions ordered by links. Most systems that assist in project planning represent plans as PERT charts. This form of representation is, however, inadequate to capture or represent the rationale(s) for the choices of actions in a plan. SIPE-2 can record the intentions and justification for specific actions, as well as their effects, and utilizes this knowledge to build a more complex dependency network that captures the rationale(s) of a plan.<sup>‡</sup> This knowledge is an essential component of the dynamic replanning capabilities that will be described in greater detail in Section 3.



**Figure 2. Hierarchical Planning**

<sup>\*</sup>SIPE-2 is proprietary software, developed and licensed by SRI International. All product and company names mentioned in this document are the trademarks of their respective holders.

<sup>†</sup>SIPE-2 is implemented in LUCID Common Lisp, running under the Sun Microsystems, Inc. (Sun) operating system, SunOS 4.1.3. SIPE-2 also utilizes the LUCID Common Lisp Interface Manager, CLIM version 1.0.

<sup>‡</sup>Thus, SIPE-2 can be described as an intelligent PERT-chart builder, although it does provide many other capabilities.

SIPE-2 can also represent spill response procedures and operations at multiple levels of detail. A high-level representation may be useful for ensuring that no major parts of the response plan are missing, whereas lower-level representations show exactly which resources are being utilized within the plan. The number of planning levels can be increased or decreased as needed. Figure 2 depicts the development of the plan from level 1 to level N. At each level, different pieces of information are applied to the current situation, the applicability of specific response operations, or their duration and effectiveness. Thus, SIPE-2 manages the integration of the relevant information hierarchically and without confusion.

During the planning process, SIPE-2 keeps track of a great deal of information, and presents the user with choices of procedures or operations, resources, locations, and/or times, where such choices exist. These choices are presented in lists, which are not prioritized but have been checked to ensure the efficacy and appropriateness of every item. For instance, in presenting choices of operations, SIPE-2 will already have ascertained that they produce the necessary effects, and meet the applicability conditions for the current problem. In choosing appropriate response equipment, SIPE-2 checks whether the equipment can withstand the operating environment. In this way, SIPE-2 guides the selection of planning choices, but requires the user to make the final choice.\*

At the end of each planning level, SIPE-2 checks the plan for consistency, ensuring that no actions undo the effects of others, and that no temporal or resource conflicts exist among concurrent branches of the plan. Examples of these conflicts are the placing of a boom across a harbor to prevent access to the harbor for offloading skimmed oil, the arrival of a specific piece of response equipment too late for it to be effective, or plans to use a single item of equipment at the same time in different locations. SIPE-2 can identify these conflicts and suggest how they might be resolved, either by choosing different resources, locations, and times, or by ordering the actions such that the conflict is avoided.

**Evaluation Module.** The Evaluation Module is implemented in a commercial modeling tool produced by Informix Software, Inc.'s HyperScript Tools (HSTools), as a spreadsheet that is generated by the planner. Upon completion of a plan, the user can execute a command that generates an evaluation as a spreadsheet within HSTools. The spreadsheet constructed from the plan explicitly expresses all the assumptions necessary for an evaluation. All plan operations are shown in the tables that make up the module. All constants, expressions, and functions that describe oil transport and removal are also shown in these tables, and are modifiable within HSTools, so that the user can change any part of the evaluation model and any of its assumptions without needing to modify or rerun any of the modules upon which it depends. In this way the evaluation module can be used to perform what-if analysis on the results of a scenario and on the plan generated in response to the scenario. Furthermore, the versatility of the modeling tool, and the explicit display of the entire evaluation model and its assumptions, enable the user to extend and customize the model to answer new concerns that may be addressed to it.

**Map Display Module.** The Color Map Display Module, SITMAP, provides most of the essential features of a geographic information system (GIS). The user can, for example, generate a variety of overlays to show marine preservation areas; the trajectory of an oil spill; the current locations of response equipment (its home base or current position during the response operation); the

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\*As more knowledge is captured within the planning system, it is possible for SIPE-2 to make more choices for the user. In this way, one can automate some of the more mundane choices, leaving the more complex choices to the user.

transportation routes for the movement of the response equipment to the area of operations; and the amount and location of the damage caused by the oil spill. Each of the icons that represent the above information on the map can be used to display more detailed textual information in pop-up windows. In this way, the Color Map Display Module provides the necessary capabilities to display information from the equipment and logistics planner, the trajectory and oil spill disposition model, and the evaluation module.

### **3 DYNAMIC REPLANNING**

This section describes in detail the dynamic replanning capabilities within SRCS and their application to spill response planning. Past approaches to replanning are briefly discussed and contrasted with the dynamic replanning techniques incorporated into SRCS. These dynamic replanning techniques are described in the context of a specific set of examples in which situation information rapidly changes.

#### **3.1 PAST APPROACHES TO REPLANNING**

Past approaches to rapidly changing input information, especially within operations research (OR), have required that entire OR algorithms be rerun with the newly revised input parameters. This process is not only time consuming but also performs redundant computations on parts of the problem that are not affected by the revised input parameters. Because relationships and dependencies between different parts of the problem and solution description are not represented in typical OR algorithms, it is difficult to discern which parts of the problem and solution descriptions are affected by the changing parameters, without rerunning the entire OR algorithm. Thus, OR techniques are a limited means of performing efficient computations within dynamic environments. PERT charts and critical path analysis (CPA) methods also are limited means of generating plans that can be easily modified as a situation changes.

#### **3.2 TECHNOLOGY TRANSFER FROM DOD-FUNDED CONTRACTS**

In this section we describe the use of the dynamic replanning techniques being developed by SRI under DoD contracts for military operations planning. These contracts have been funded under the Advanced Research Projects Agency (ARPA)/Rome Laboratory Planning Initiative (ARPI), a program conducted for the DoD's ARPA and the USAF's Rome Laboratory.

Under two of these contracts (SRI Projects 2062 and 4636), we have been developing methods for revising military crisis response plans in response to changes in the situation, such as changes in enemy threats; the changes in the availability of, or the destruction of friendly forces and equipment; the disruption of transportation routes; and the failure of planned actions. There are many similarities in planning responses to military threats and oil spills. Both problems require the deployment of a large quantity of equipment, personnel and other resources that must work together to meet operational needs. Thus, it has been possible to successfully transfer advanced technology developed under these DoD contracts to meet USCG needs for spill response planning.

We estimate the equivalent value of the developed technology that is directly applicable to the tasks within this research grant to be more than \$400,000. This figure also includes a contribution from SRI's Internal Research and Development funds. The value of SRI's research and

development efforts associated with this technology since the early 1990s is in the range of \$4–5 M, with a further \$2–3 M proposed for the next 3 years. Hence, the benefits to the USCG of the continued transfer of technology from DoD contracts to USCG applications for spill response planning and other related tasks can be substantial.

### 3.3 UNDERLYING DYNAMIC REPLANNING TECHNIQUES

The power of the dynamic replanning techniques within SRCS is derived primarily from the knowledge contained within the complex network of dependencies between the actions within a plan. This knowledge captures the *intentions* and *justifications* for the actions within the plan, often called the *plan rationale*; this rationale is used effectively during replanning to highlight the consequences to the dependencies within the plan of changes in the conditions input into the plan, represented by environmental and other situation parameters.

#### 3.3.1 Plan Rationale

The plan rationale comprises knowledge in the following forms:

- **Preconditions**, representing the *applicability* of specific actions, operations and procedures within a plan
- **Effects**, representing the *consequences* of specific actions, operations and procedures within a plan
- **Dependency links**, denoting *relationships* primarily between the effects and preconditions of two or more nodes in a plan, and secondarily between nodes in different hierarchical levels of the plan
- **Typed arguments**, indicating the *inheritance* of properties from a parent object to subordinate classes of objects, which may be constrained further for specific nodes in a plan, and the *allocation* of resources and times to nodes within a plan.

#### 3.3.2 Preconditions

Preconditions, represented by predicates of the form, (*pred arg1 arg2 . . . argN*), describe applicability conditions for planning operators that translate goals within a plan into networks of subgoals and specific actions, or procedures. If the preconditions for a specific operator are not met, then the network of subgoals or action, called the *plot* of an operator, is not introduced into the plan network. The preconditions act as constraints not only on the choice of the operator used to solve a specific goal, but also on the acceptable choices, or instantiation, of arguments that may be introduced into the plan. Thus, the preconditions are also a method for introducing specific information from the current state of the world into the plot of an operator at the appropriate level of detail. This information may take the form of specific instantiations of arguments with objects in the world, or the posting of further constraints on the choices of these objects.

For example, the preconditions for a boom employment operator may be that the chosen boom must be appropriate for the predicted environmental conditions at the location where the boom will be deployed. Such parameters or threshold values may be represented by the values for the *sea state*, which may be either quantitative, numerical values or qualitative values such as protected, calm, choppy, or rough sea.

When the situation changes, specific predicates describing the state of the world also change, which may invalidate the preconditions for several operators employed in the planning process. As a result, the subgoals and actions introduced by these operators may need to be removed from the current plan. For example, if the weather conditions deteriorate and raise the values for the sea-state predicate, then some of the choices of boom may be inappropriate because they are suitable only for calm or protected waters. As a result, the preconditions for the operations that make use of these booms will be invalidated. Thus, the planner knows which parts of the response plan should be revised and modified.

### 3.3.3 Effects

Effects, like preconditions, are represented by predicates of the form *(pred arg1 arg2 . . . argN)*; they describe the consequences of introducing specific actions or procedures. In a sense, effects add new or derived predicates into a plan beyond the input conditions that highlight the contribution of the actions or procedures that modify the state of the world. For example, the effects of deploying a specific skimmer in a particular location are that its skimming capacity is now available to reduce the oil left on the water by an amount based on various parameters associated with the skimmer, such as the pump capacity, spill encounter rate, type of oil, and environmental conditions. The effects may refer to the planning operator as a whole or to the individual subgoals or actions within their plots. Thus, if a specific operator is removed from a plan because of invalidated preconditions, then the relevant effects also must be removed.

### 3.3.4 Dependency Links

The dependency links within a response plan denote not only how the operations are dependent upon each, but also which specific input conditions or derived effects satisfy the preconditions of the relevant operations. In other words, the dependency links are the glue between all the components of a response plan, and represent an important part of the plan rationale. As the situation changes and the plan is revised, some dependency links are removed and other new ones added. A number of dependency links can be represented. Currently, we are using the simplest form of dependency links, which represent the *before* and *after* relationships between the operations, i.e., the order in which the operations should be performed).

Other dependency links include the following relationships:

- **During**—An operation must be performed entirely within the period of performance of another operation: e.g., for effective skimming, a weir skimmer should be employed *during* the period in which containment is provided by a boom system.
- **Overlaps**—One operation overlaps another: i.e., the second operation starts before the first has been completed: e.g., the period of protection provided by a diversion boom for one sector must *overlap* the period of protection provided by another boom in an adjacent sector.
- **Starts/ends**—One operation starts or ends exactly at the same time as another: e.g., skimmers and storage devices such as bladders must be in place and ready to begin operation at the same *start* time and finish at the same *end* time.
- **Meets**—One operation begins immediately after another, with no time gap between the two operations.

### 3.3.5 Typed Arguments

Most typed arguments are associated directly with specific operations, and represent the following types of information:

- **Inheritance** of properties from parent to subordinate classes of objects that denote constraints on the choices of resources for operations: e.g., the class of objects representing booms have similar properties and all belong to the parent class of response equipment. There are many subclasses of booms with different properties, such as fenced booms, which tend to be rigid; or curtain booms, which may be filled with foam or may be self-inflating.
- **Allocation** of resources to specific operations, and the ability of specific resources to be shared among other operations in the response plan: e.g., the vacuum trucks allocated to a sector of shore may be shared with the operation to clear an adjacent sector.
- **Temporal information** concerning the allocation of start and end times, durations, and time windows to specific operations: e.g., the earliest start time of a skimming operation may be linked or dependent on the deployment of a containment boom in a specific sector of sea.

Each of these typed arguments is posted at the appropriate level in the response plan, and may be further constrained by changes in the situation.

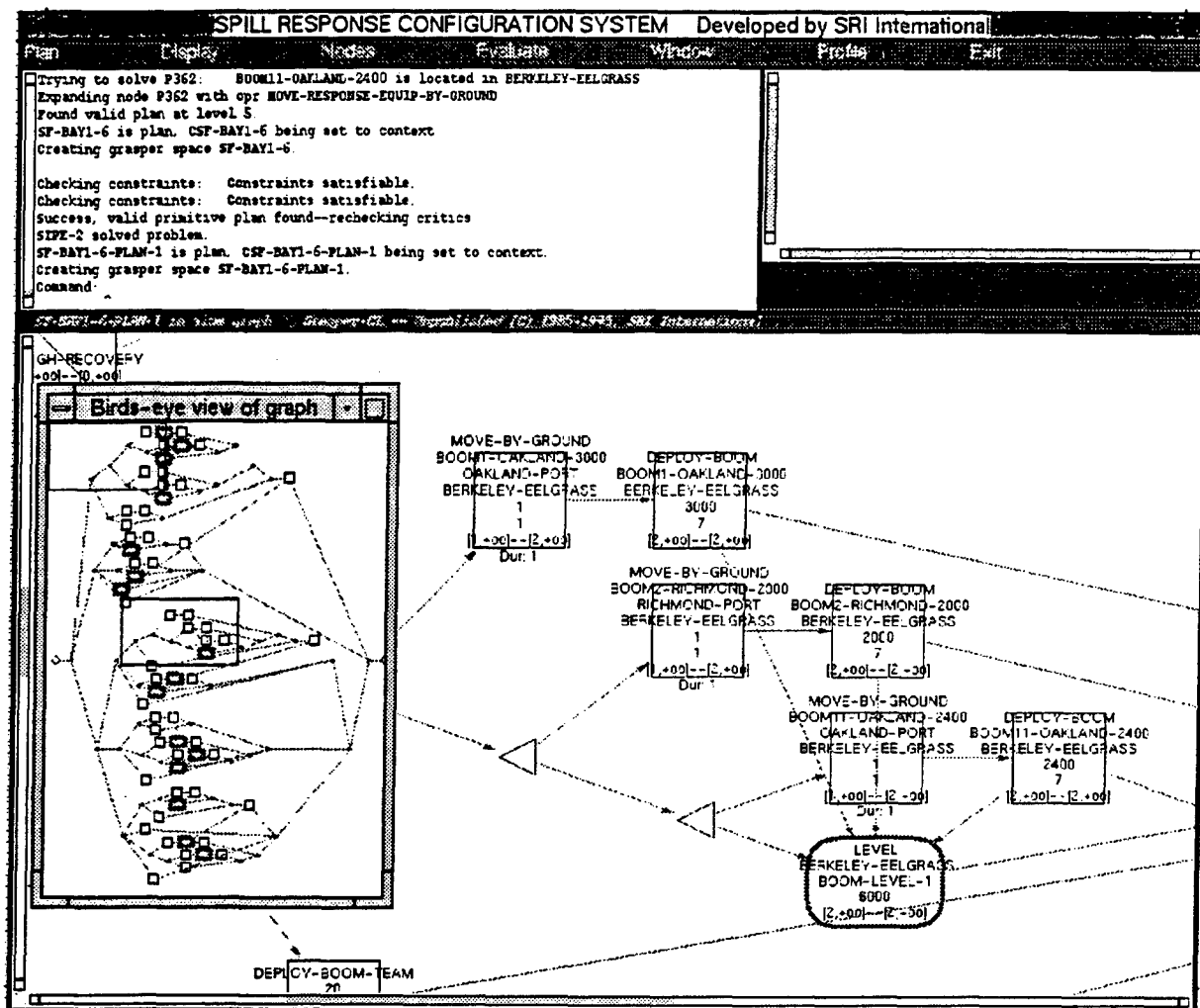
### 3.4 SPECIFIC REPLANNING EXAMPLES

When the situation information changes, SRCS checks to see that operations within the plan are still applicable and consistent with each other. If not, then SRCS uses the plan rationale to identify those parts of the plans that are affected by the changes and presents choices to the user to remedy the situation change. For instance, the severity of the weather conditions might affect the effectiveness of specific booms and, as a result, different booms able to work under the new operating conditions may be required.

Figure 3 shows a screen display taken from the San Francisco Bay spill scenario demonstrated previously to several USCG MSOs. Three booms chosen to provide protective diversion booming for the BERKELEY-EELGRASS sensitive area., i.e., BOOM-1, BOOM-2, and BOOM-11. The first two booms can operate in severe sea states. BOOM-11, however, is effective only in protected or calm waters. When the sea-state values are increased above the threshold for BOOM-11, but below those for BOOM-1 and BOOM-2, SRCS determines that the operations that make use of BOOM-11 are invalid and should be removed from the response plan.

Figure 4 shows the resulting response plan. Note that the oval-shaped node is no longer highlighted with a dark border. Indeed, the color display shows that the outline of this oval-shaped node has changed from black to a turquoise blue, with a corresponding change in color of the text within this node. The new colors signify that the objective to obtain 6000 feet of boom for the diversion booming operation at BERKELEY-EELGRASS is now no longer completely satisfied.

Figure 5 shows the addition of BOOM-3 to the response plan. This boom provide the necessary additional boom to complete the diversion booming requirements for that sensitive area.



**Figure 3. Boom Choices Prior to Replanning**

These three figures illustrate, in one simple example, how SRCS permits the user to explore the effects of changes in the situation upon previously planned choices, and guides the user to make appropriate changes to the plan.

### 3.5 VARIANT REPLANNING SCENARIO

SRI has also completed the development of a variant on the San Francisco Bay spill scenario to demonstrate the full dynamic replanning capabilities of SRCS. This variant is based on the changes to the original Harding Rock scenario that were discussed during the Response Strategy Working Group Meetings of the San Francisco Area Committee, during 1994.



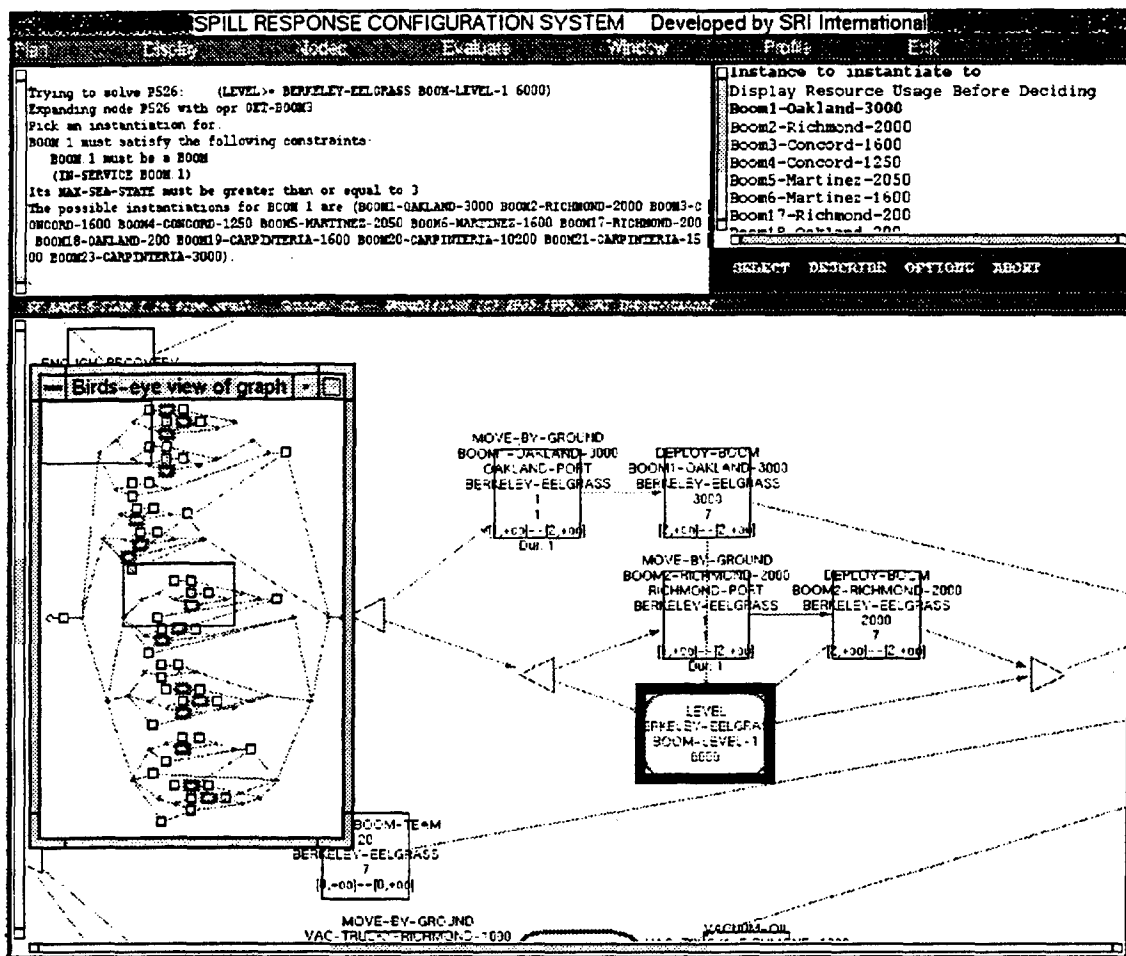


Figure 4. Invalidated Boom Choice Removed from Plan

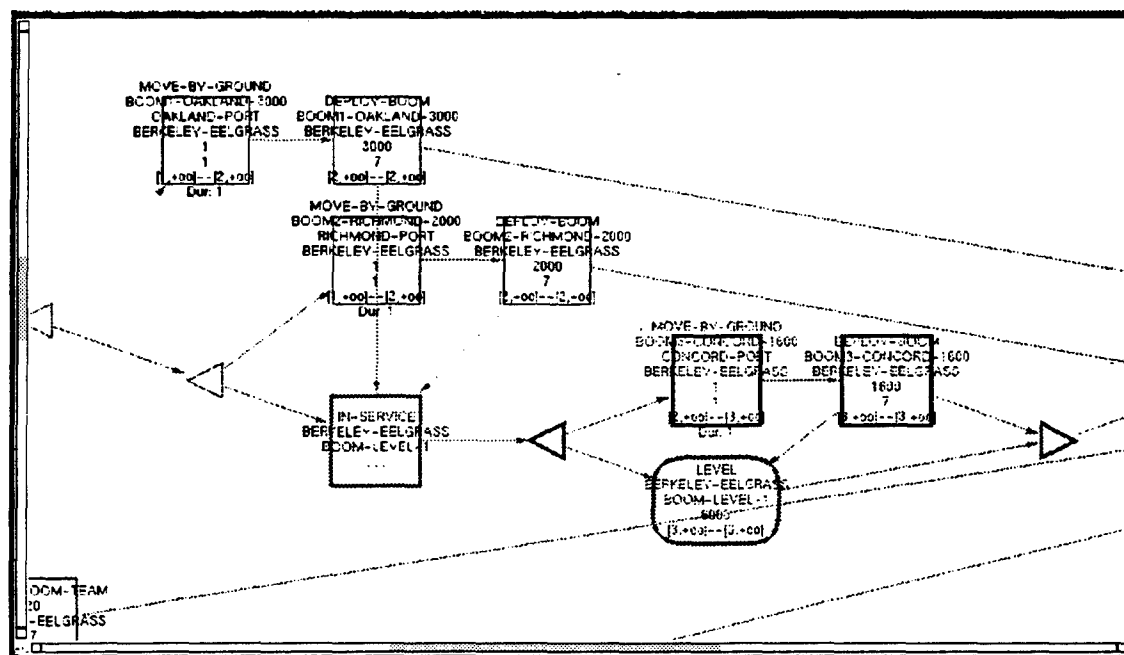


Figure 5. Completely Revised Boom Choices

This variant replanning scenario was demonstrated at the International Oil Spill R&D Forum, at the International Maritime Organization, London, UK, at the end of May 1995. The variant scenario was also demonstrated at the USCG Oil Pollution Research Grant Presentations held at VNTSC, 9–10 August 1995. Appendices A and B contain screen shots of the demonstration and prints of the accompanying viewgraphs.

## 4 KNOWLEDGE-BASE MAINTENANCE

In this section we describe the user-interface capabilities for revising and updating the knowledge base that were added to SRCS under this contract. These new capabilities enable the user to expand and extend the knowledge base as new response methods are developed, or as new equipment capabilities are provided by spill-response-equipment manufacturers.

The underlying knowledge and database that SRCS utilizes during the planning process comprises information about the following:

- Spill-response resources, such as their location, type, and quantity, as well as other more detailed information about their operating conditions and capabilities
- Spill-response operations, such as the use of booms, skimmers, and vacuum trucks
- Geographic information about the surrounding shores and sea sectors, such as the location of sensitive areas, equipment storage sites, and sea and ground transports, as well as data on the water temperature, wind, and tides
- Spill incident data, such as discharge rates and quantities, as well as the location and time of the initial spill.

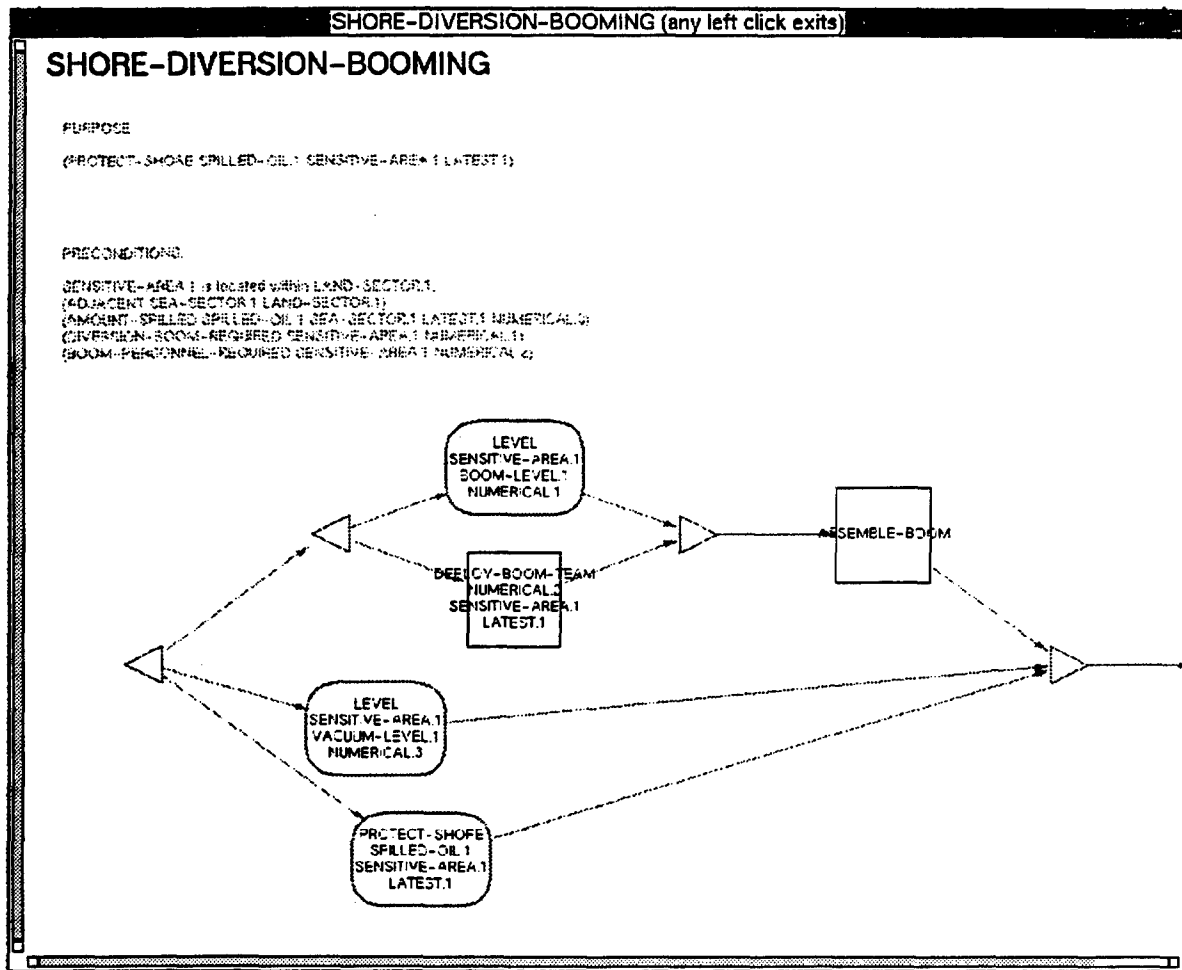
The enhanced user interface now comprises several graphical editors for refining spill-response operations and methods (the operator editor); for modifying scenario parameter, such as weather conditions (the predicate editor); and for adding new equipment and personnel (the resources editor). Each of these editors is a structured, graphical editor that highlights the available choices and prompts the user for responses.

The operator editor enables the user to

- Revise the preconditions for spill operations and methods, and their effects
- Add new steps to the procedures for using the response methods
- Highlight other constraints on the choices of equipment types for these operations.

Figure 6 shows an example of the *SHORE-DIVERSION-BOOMING* operator. With the aid of the operator editor, the user may now modify this operator by adding actions or subgoals to this operation; revising the applicability conditions (or preconditions) for this operation; or changing the effects of some of the actions.

The predicate editor enables the user to change a variety of scenario-specific parameters including the effects of weather conditions on sea state, wave height, and water temperature; the size, location, direction, and discharge rate of the spill; and the availability of response equipment, personnel, and transportation equipment. These parameters are accessible through a multipane window with structured editing capabilities that guide the user to make acceptable changes to the knowledge base.



**Figure 6. Operator Editor Display of Shore-Diversion-Booming Operator**

Figure 7 shows the predicate editor with a display window comprising six panes highlighting the predicates that describe the current state of the scenario. The predicate editor guides the user to add, delete, or revise existing or new predicates. This editor is also used for replanning tasks—especially for changing the situation information.

The resources editor shows the hierarchical structure of the available equipment and personnel, highlighting the properties associated with each resource in the knowledge base. The values of the parameters for the operating conditions for the equipment may be revised, new equipment and personnel may be added or deleted, and relationships between resources and constraints on their use may be modified.

Figure 8 shows part of the response equipment hierarchy, including some of the available booms. The resources editor (denoted "Gkb-editor" in the figure) is currently undergoing further development and is not fully integrated into SRCS.

Predicate Editor	
Command: _____	
Copy Predicate	Delete Predicate
Edit Predicate	New Predicate
Options	Exit Pred Editor
<b>COVERED SECTOR</b> (COVERED-SECTOR SF-BAY-SPILL NORTH-ALAMEDA-COAST 3) (COVERED-SECTOR SF-BAY-SPILL SF-NORTH-COAST 1) (COVERED-SECTOR SF-BAY-SPILL GOLDEN-GATE 7) (COVERED-SECTOR SF-COAST-SPILL WEST-MARIN-COAST 12) (COVERED-SECTOR SF-COAST-SPILL GOLDEN-GATE 12) (COVERED-SECTOR SF-COAST-SPILL PACIFICA-COAST 24) (COVERED-SECTOR SF-COAST-SPILL MOSS-BEACH-COAST 36) (COVERED-SECTOR SF-COAST-SPILL PESCADERO-COAST 48) (COVERED-SECTOR SF-COAST-SPILL ANO-NUEVO-COAST 72)	<b>THREATENED SHORELINE</b> (THREATENED-SHORELINE SF-BAY-SPILL BERKELEY-BELGPASS 7) (THREATENED-SHORELINE SF-BAY-SPILL RODEO-LAGOON 11) (THREATENED-SHORELINE SF-BAY-SPILL YERBA-BUENA-ISLAND 4) (THREATENED-SHORELINE SF-COAST-SPILL PESCADERO-BEACH 48)
<b>SEA STATE</b> (SEA-STATE SF-NORTH-COAST 0 2) (SEA-STATE NORTH-ALAMEDA-COAST 0 1) (SEA-STATE EAST-MARIN-COAST 0 2) (SEA-STATE GOLDEN-GATE 0 3) (SEA-STATE SF-NORTH-COAST 1 2) (SEA-STATE NORTH-ALAMEDA-COAST 1 1) (SEA-STATE EAST-MARIN-COAST 1 2) (SEA-STATE GOLDEN-GATE 1 3) (SEA-STATE SF-NORTH-COAST 2 2) (SEA-STATE NORTH-ALAMEDA-COAST 2 1) (SEA-STATE EAST-MARIN-COAST 2 2) (SEA-STATE GOLDEN-GATE 2 3) (SEA-STATE SF-NORTH-COAST 3 2)	<b>OK SEA STATE</b> (OK-SEA-STATE SF-NORTH-COAST 0 2) (OK-SEA-STATE SF-NORTH-COAST 0 3) (OK-SEA-STATE SF-NORTH-COAST 0 4) (OK-SEA-STATE SF-NORTH-COAST 0 5) (OK-SEA-STATE SF-NORTH-COAST 0 6) (OK-SEA-STATE NORTH-ALAMEDA-COAST 0 1) (OK-SEA-STATE NORTH-ALAMEDA-COAST 0 2) (OK-SEA-STATE NORTH-ALAMEDA-COAST 0 3) (OK-SEA-STATE NORTH-ALAMEDA-COAST 0 4) (OK-SEA-STATE NORTH-ALAMEDA-COAST 0 5) (OK-SEA-STATE NORTH-ALAMEDA-COAST 0 6) (OK-SEA-STATE EAST-MARIN-COAST 0 2) (OK-SEA-STATE EAST-MARIN-COAST 0 3)
<b>EQUIPMENT LOCATIONS</b> TUG-1 is located in MISO-SF-BAY-PORT. TUG-2 is located in MONTEREY-PORT. AIRCRAFT-1 is located in HALF-MOON-AIRFIELD. AIRCRAFT-2 is located in ALAMEDA-AIRFIELD. VAC-TRUCK1-RICHMOND-1000 is located in RICHMOND-PORT. VAC-TRUCK2-RICHMOND-1000 is located in RICHMOND-PORT. VAC-TRUCK3-SF-1000 is located in SAN-FRANCISCO. VAC-TRUCK4-SF-1000 is located in SAN-FRANCISCO. VAC-TRUCK5-SF-1000 is located in SAN-FRANCISCO. VAC-TRUCK6-SF-1000 is located in SAN-FRANCISCO. VAC-TRUCK7-SF-1000 is located in SAN-FRANCISCO. VAC-TRUCK8-SF-1000 is located in SAN-FRANCISCO. TRACTOR-1 is located in SAN-FRANCISCO.	<b>AVAILABLE EQUIPMENT</b> (AVAILABLE TUG-1 3) (AVAILABLE TUG-2 3) (AVAILABLE AIRCRAFT-1 1) (AVAILABLE AIRCRAFT-2 1) (AVAILABLE VAC-TRUCK1-RICHMOND-1000 1) (AVAILABLE VAC-TRUCK2-RICHMOND-1000 1) (AVAILABLE VAC-TRUCK3-SF-1000 1) (AVAILABLE VAC-TRUCK4-SF-1000 1) (AVAILABLE VAC-TRUCK5-SF-1000 2) (AVAILABLE VAC-TRUCK6-SF-1000 2) (AVAILABLE VAC-TRUCK7-SF-1000 2) (AVAILABLE VAC-TRUCK8-SF-1000 2) (AVAILABLE TRACTOR-1 1)

Figure 7. Predicate Editor Display

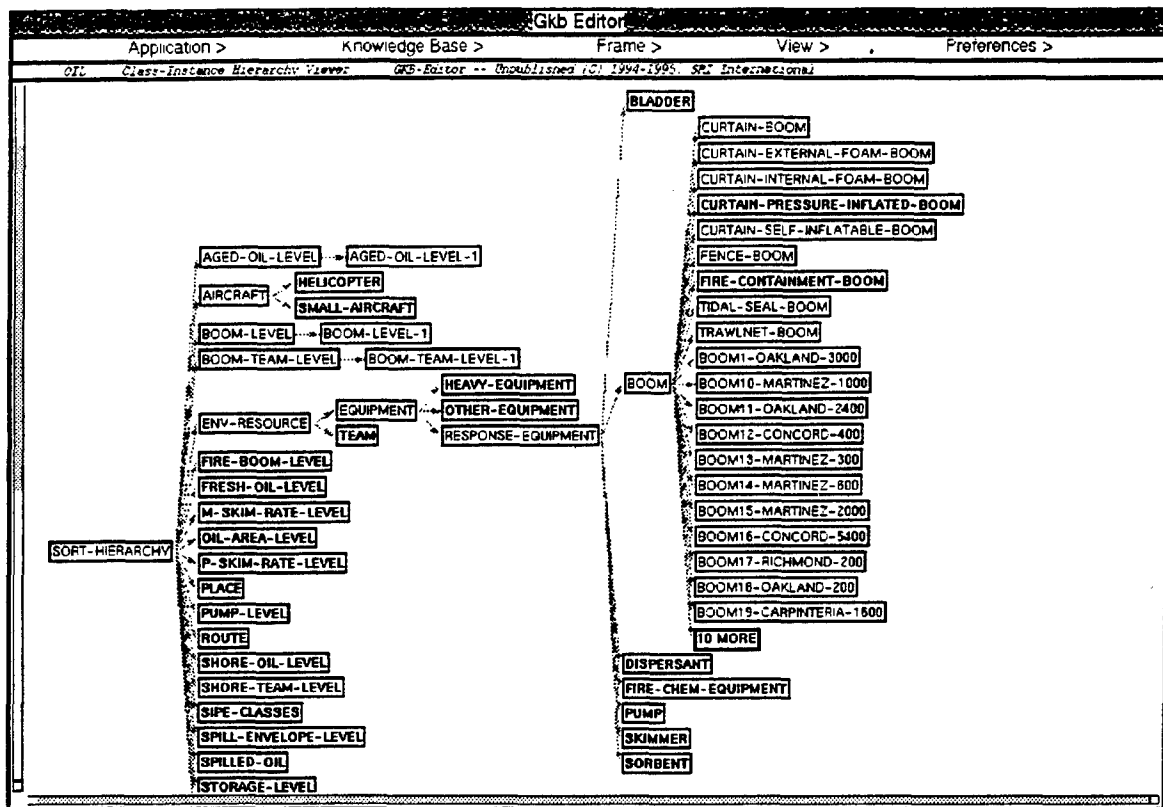


Figure 8. Display of the Resources Editor

## 5 CONCLUSIONS

In the current spill response domain, we have demonstrated the suitability and extensibility of this technology as a decision support tool for spill response configuration planning. We have shown how dynamic replanning techniques provide additional capabilities for guiding the process of revising the response plan as a result of changing situation information. We have also described how structural graphical editors can be used to assist the user in updating and enhancing the knowledge and databases that form an important part of SRCS.

The capabilities within the underlying AI planning technology within SRCS, that is, SIPE-2, are continually being expanded under DoD contracts, incorporating more sophisticated technology for distributed reasoning, planning in uncertain environments, and machine learning.

Having successfully demonstrated SRCS for a range of configuration planning tasks, the system is ready for wider application and validation. Further, with developments in the underlying technology, SRCS will be able to take on new challenges. We review some of these possibilities below.

### 5.1 MEETING COAST GUARD PLANNING NEEDS

The objective to which we were tasked is the configuration of cleanup equipment as part of the need that the USGS faces to prepare and plan in anticipation of spills that might occur. These spills are described by the risk, for example, the probability of occurrence of spills of different types and sizes. SRCS is intended to be used to plan the use of equipment against a designated set of spill scenarios. From the adequacy of these plans as determined by their evaluation, better plans can be chosen, and the corresponding equipment and siting identified.

The initial objective of SRCS has been to meet the configuration need at the national level, which is the responsibility of the USCG National Strike Force (NSF), as laid out in The Oil Pollution Action of 1990 (OPA90). OPA90 calls for the NSF to maintain a National Contingency Plan. In addition, OPA90 requires regional and area contingency plans to be written and periodically updated that are consistent with each other. SRCS is well suited for contingency planning at all levels and could be applied to assist in maintaining consistency among levels.

As someone familiar with planning will recognize, the basic functionality of SRCS can be applied to the full range of contingency planning. Specifically, the ability of SRCS to work with large amounts of low-level detail makes it appropriate for Area Contingency Planning (ACP). The Area Committee is a local spill preparedness and planning body under the direction of a federal On-Scene Coordinator (OSC) made up of federal, state and local agency and other interested party representatives. In our exposure to the local Area Contingency planning process, we realized that much of the tedium of this activity could be automated with SRCS, and a better basis for evaluation of the effectiveness of plans provided to boot. We anticipate that if an SRCS system is fielded to MSOs, it will be used to supplement various planning exercises, resulting in an increase in their preparedness in the event of a spill. Vessel and facility response plans may also improve since they are required to be consistent with Area Contingency Plans. Furthermore, other agencies that must coordinate during a spill with the OSC would benefit from better configuration planning. An example is the USAF Reserve Airlift Wing, which must preposition its supplies.

## 5.2 THE RANGE OF POSSIBLE APPLICATION OF SRCS

The AI planning technology within SRCS, in conjunction with other technologies, can be applied to other applications demanded by the USCG spill response capability. These occur in training and in response planning and execution during a spill.

Training is another aspect of preparedness. The ability of SRCS to guide a user through steps in deploying and employing response equipment makes it appropriate as a training system. The knowledge base incorporated into SRCS contains valuable information from which an inexperienced user can learn about spill cleanup strategy. Such a user can work with SRCS as a training tool, building plans and then evaluating them. By experimenting with different strategies, and seeing the disposition of oil in which they result, a user can understand which strategies are most effective. Further development of SRCS in terms of a better interface and better ability to guide the user and to explain the results of the plan it generates would result in a mature training tool. These issues were explored in the concurrent SRI grant for "Development of an Oil-Spill Response Simulation System that Determines Strategies Interactively" (Grant DTRS-57-94-G-00084).

The value of a plan is exploited when it is used, so a natural extension to configuration planning is real-time planning and response. As the name of the underlying technology states, the "System for Interactive Planning and Execution" (SIPE) is intended for use both in preplanning and during execution of a plan. The planning module from SRCS would be used to bring the plan up to date as forecasts and developments from the field became available so that the plan is kept current as the spill and other contingencies during the response evolve. This will draw upon the replanning abilities that were discussed in this report, and the ability to plan which observations are most valuable, an issue discussed in the previously mentioned concurrent SRI grant.

A response system places much larger demands on software than a configuration system, in terms of reliability, responsiveness, and soundness and completeness of data. Development of a spill response system would require additional development of both the software and knowledge base of the current system. In addition, a response system has numerous functions in addition to planning, in terms of situation display, tracking and communication. By adding a real-time planning and execution module based on the SRCS technology to a spill command and control system the spill's Incident Command Structure actions could be on a proactive footing almost immediately after an incident occurs.

Finally, it is clear that spill response is just one of numerous planning-based missions to which one might anticipate the application of AI planning technology. Whenever there is a mission that requires complicated movement of equipment and resources under time and availability constraints, this technology is a candidate for application to improve it.

## **Appendix A**

### **SCREEN DISPLAYS FOR IMO AND VNTSC DEMONSTRATIONS**



Plan
Display
Nodes
Evaluate
Window
Profile
Exit

```

Loading file socap:oil:spill-init-preds.sipe
Made changes in world P2, doing deductions.
Loading file socap:oil:spill-traj-preds.sipe
Made changes in world P2, doing deductions.
Loading file socap:oil:spill-oprs.sipe
Loading file socap:oil:spill-deduct.sipe
::: Loading binary file "/socap2/project/socap/irpout/oilspill/spill-oprs-functions.shin"
572 new predicates deduced this round.
Loading file socap:oil:spill-prebs.sipe
Command: :Socap Display Mode
Creating grasper space SF-BAY1.
Command:

```

SF-BAY1

Birds-eye view

SF-BAY1

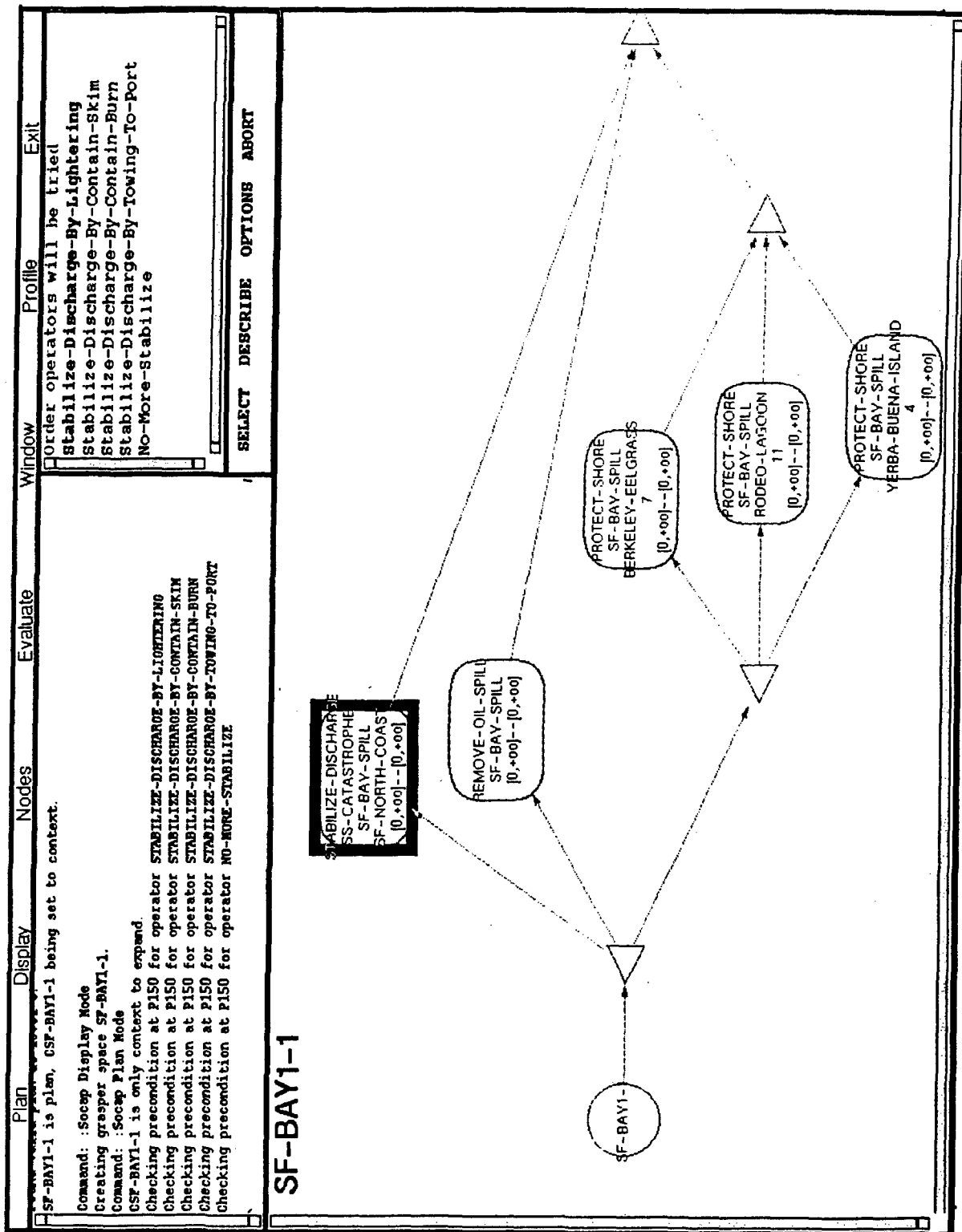
RESPOND-TO-SPILL

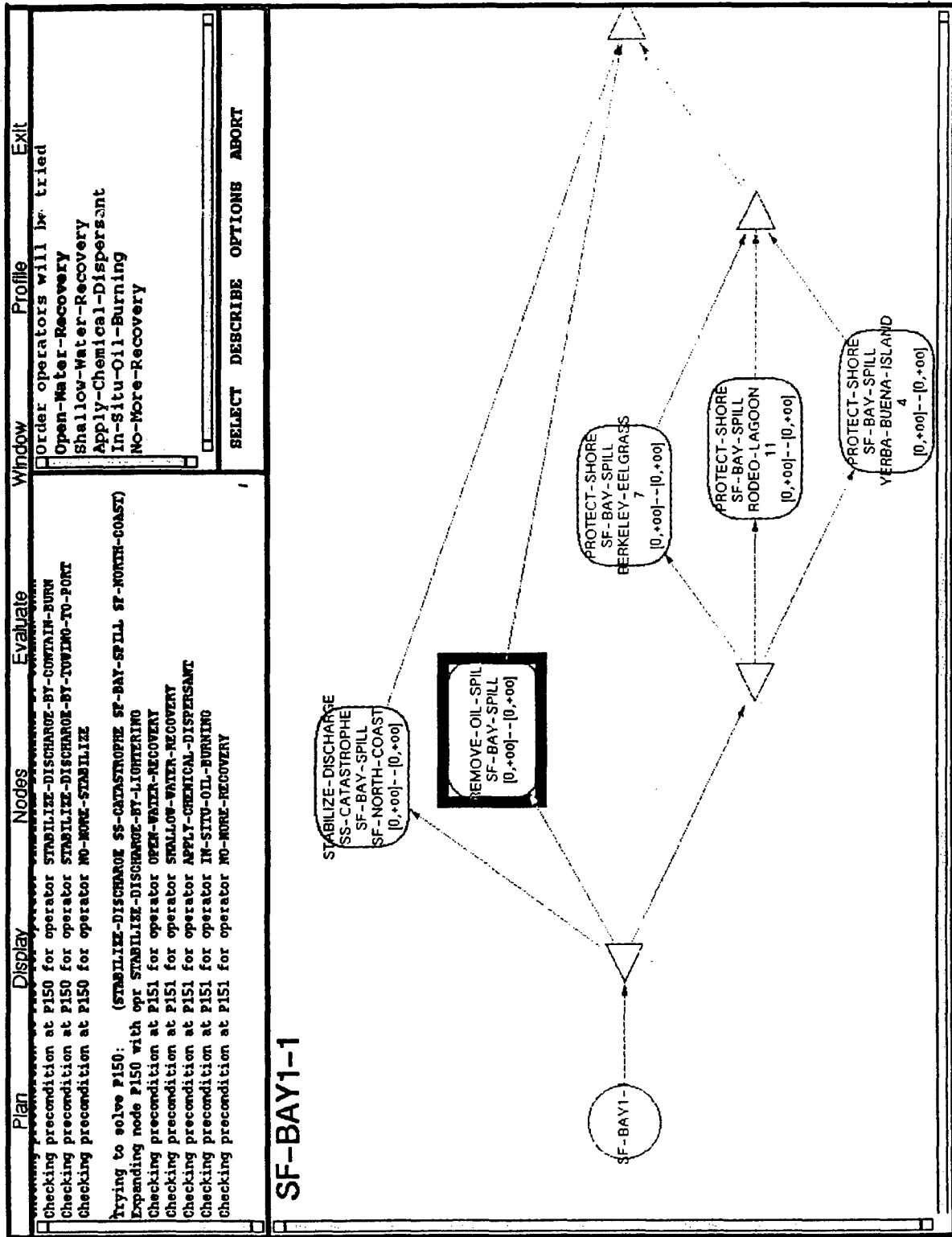
SF-BAY-SPILL

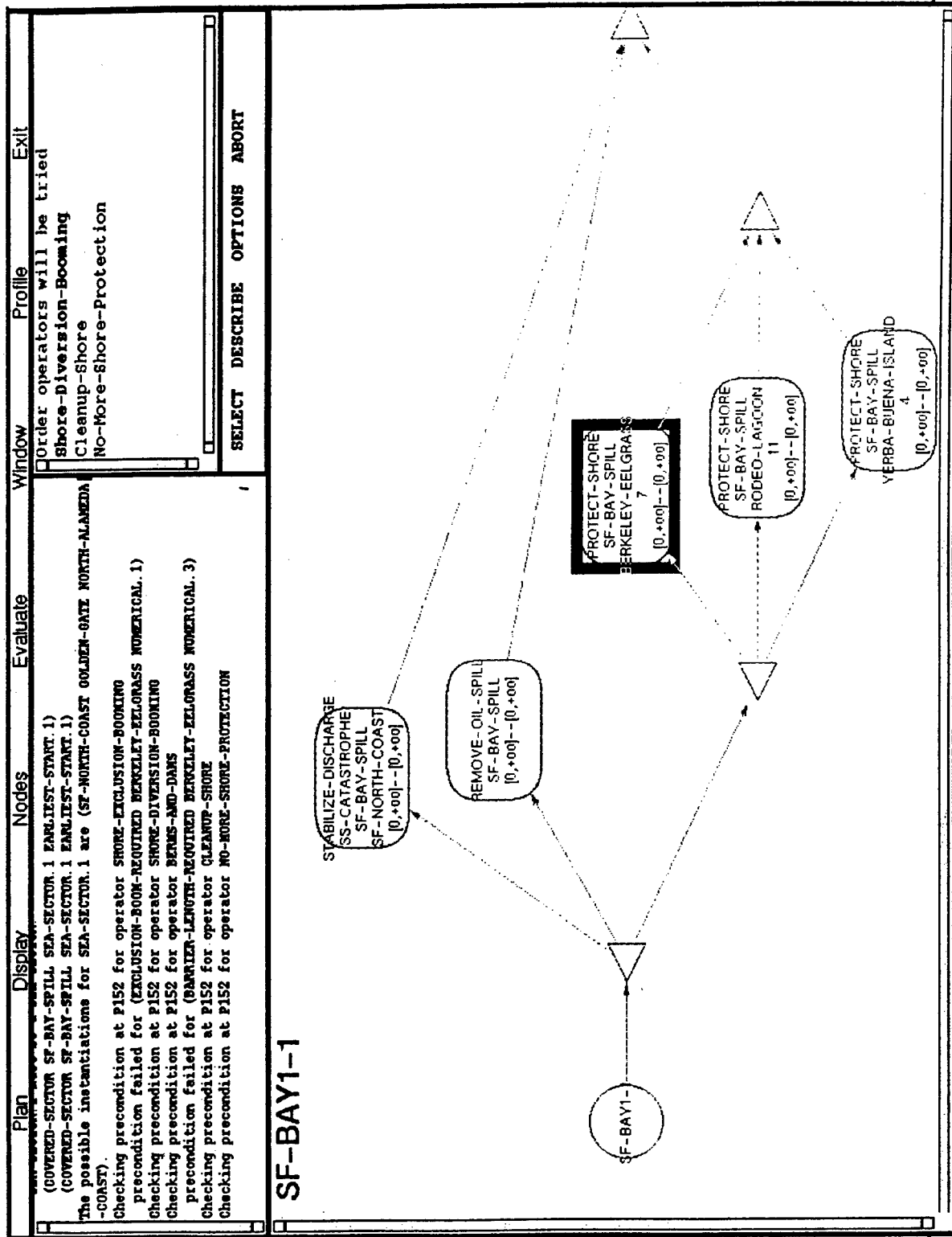
SF-NORTH-CCAST

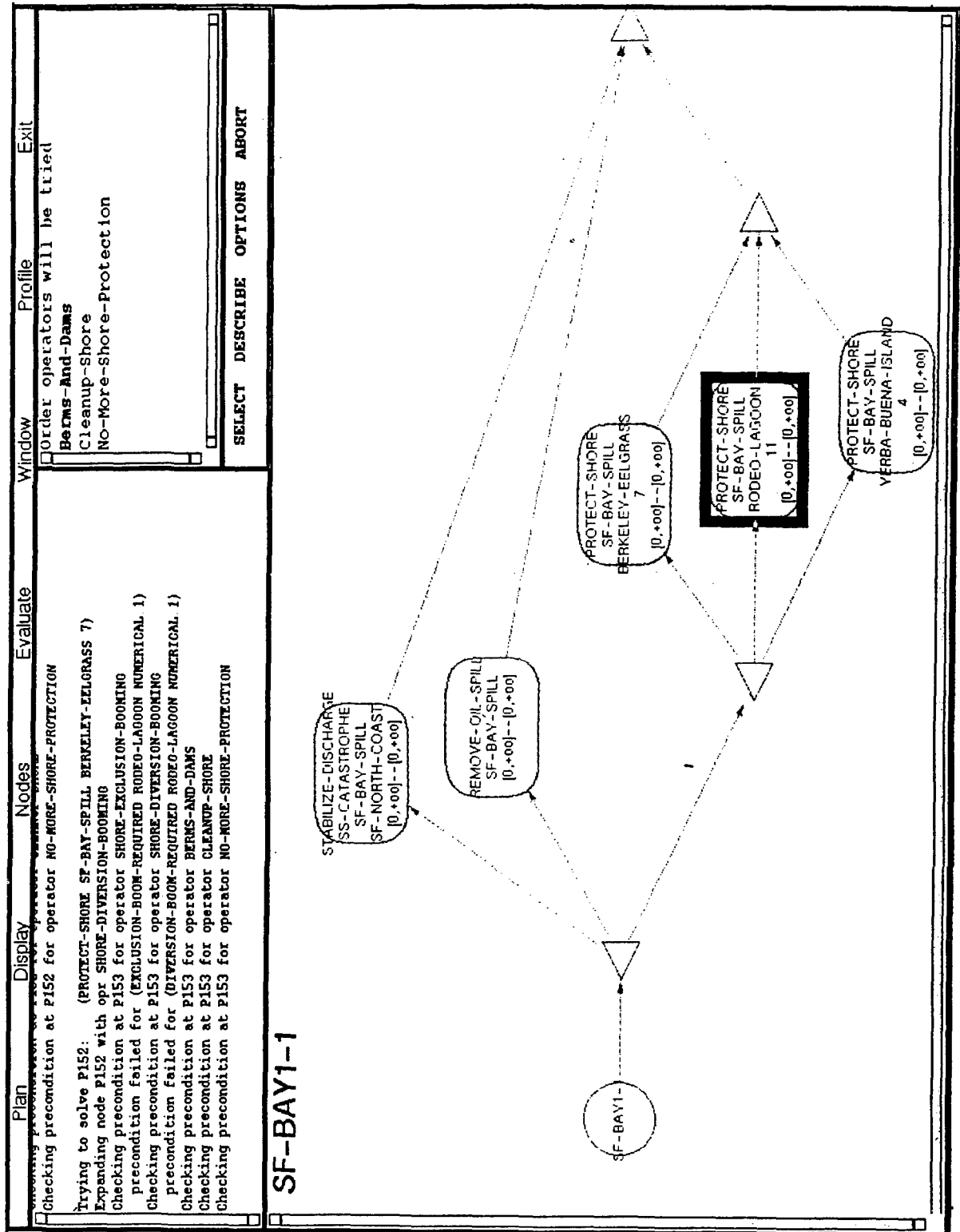
SS-CATASTROPHE

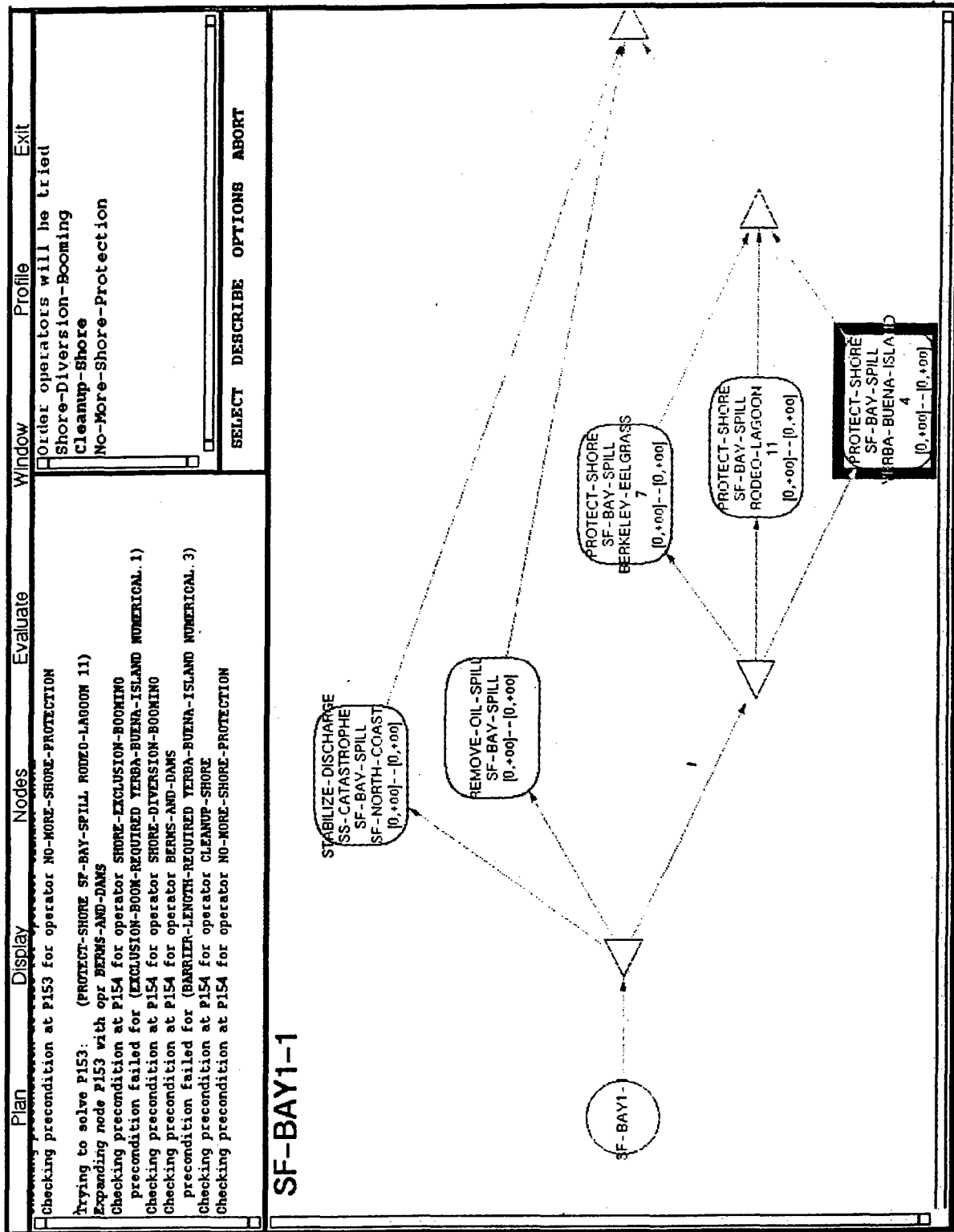
END

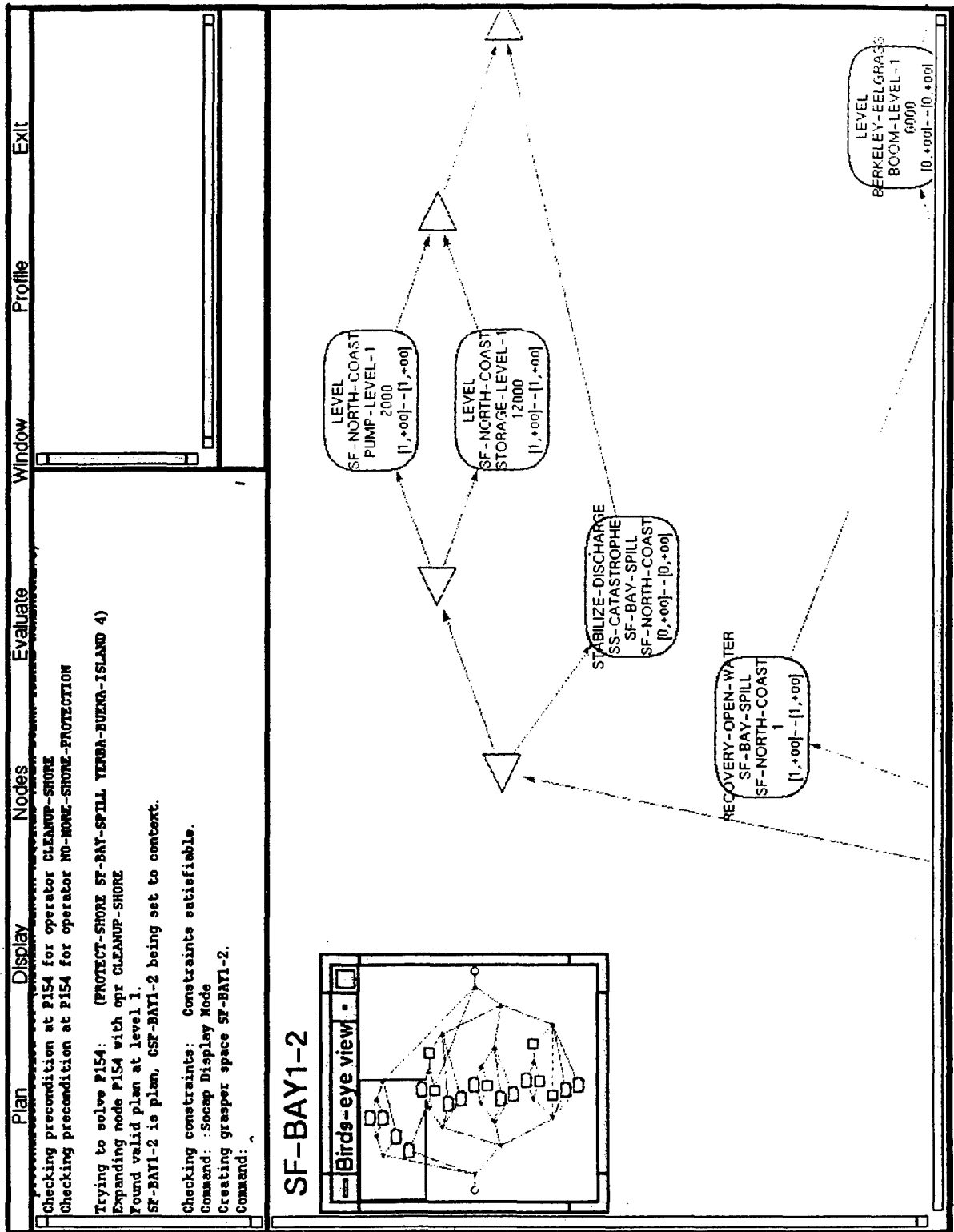


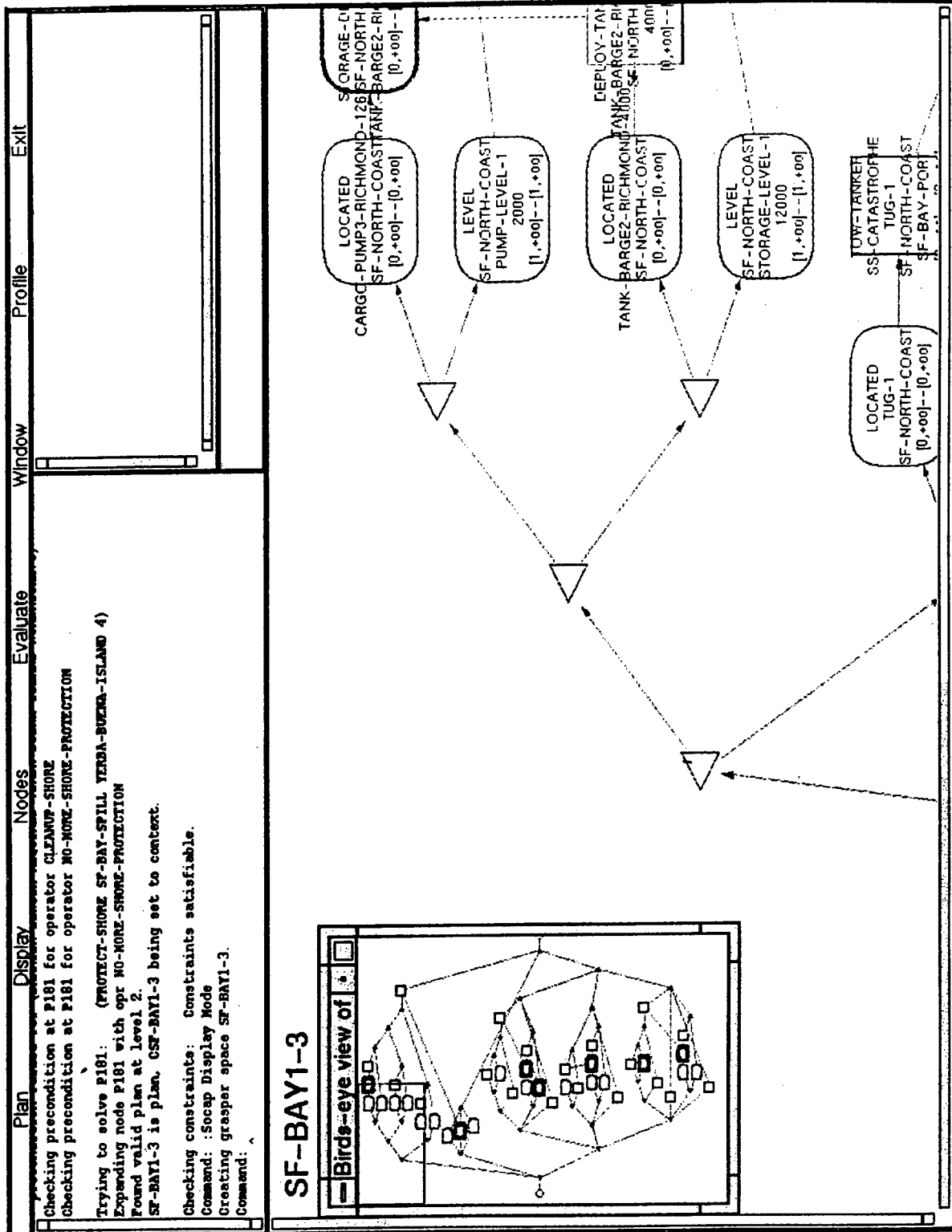




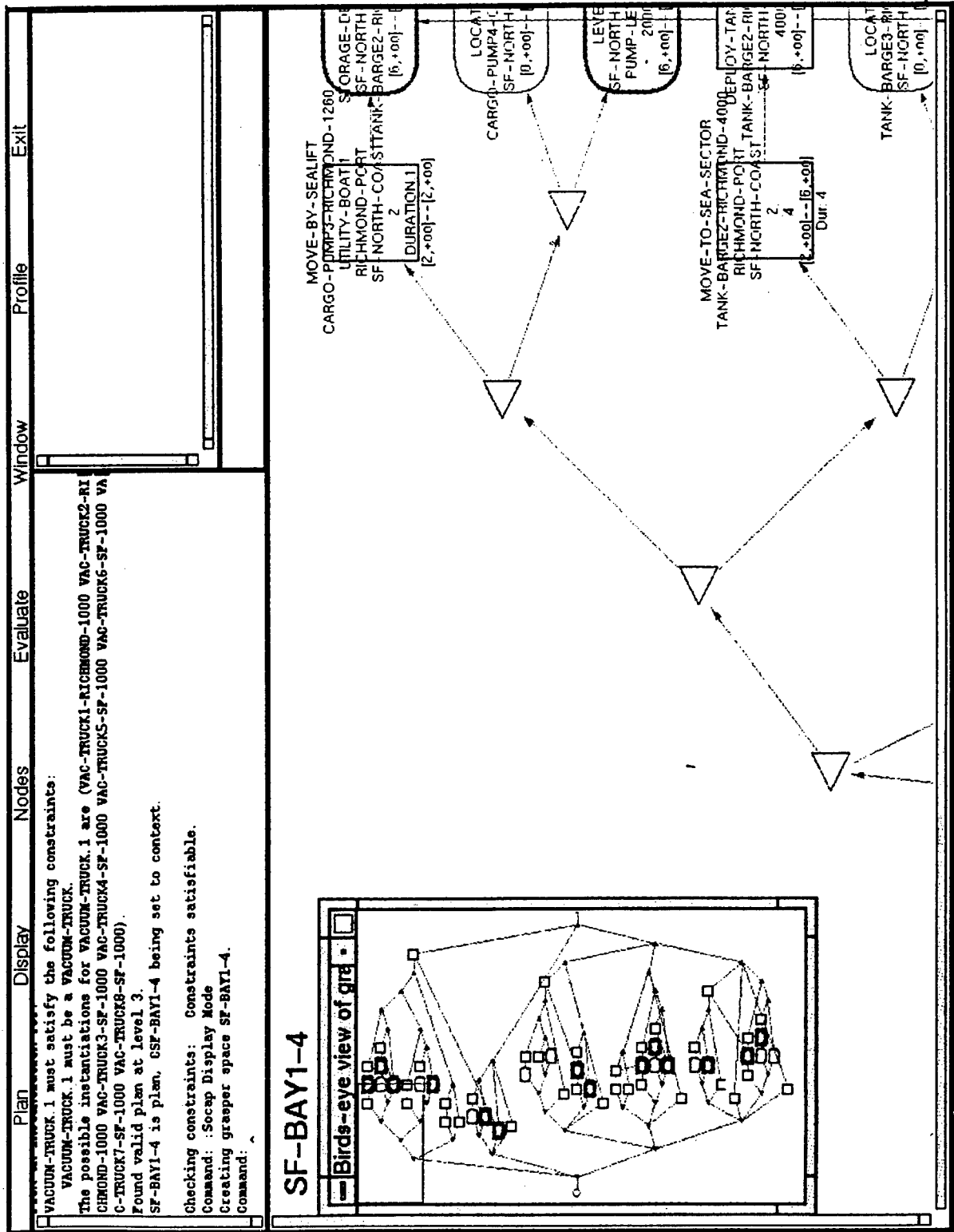




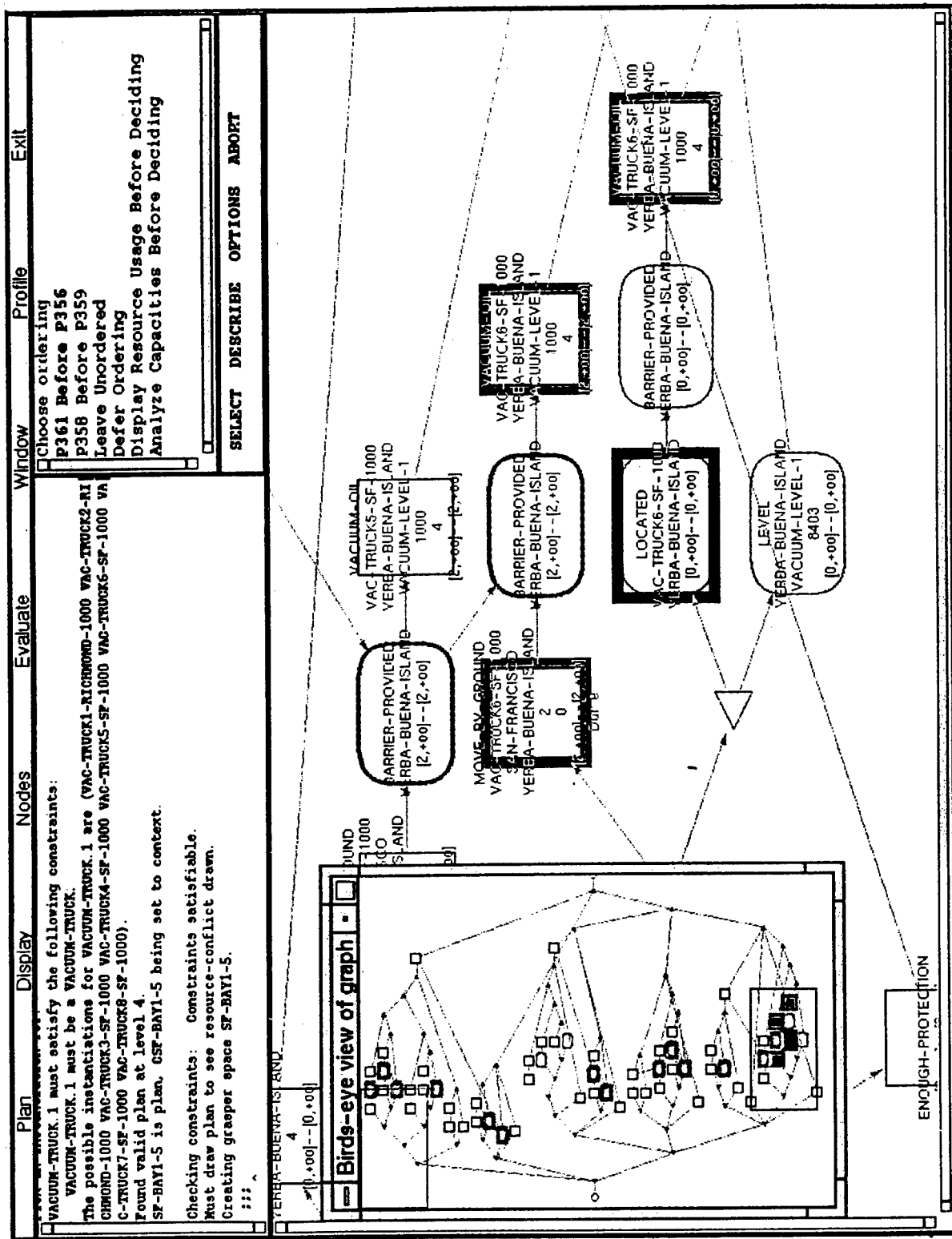








Plan	Display	Nodes	Evaluate	Window	Profile	Exit																																																
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>Expanding node P272 with opr 02T-BOOM3 Pick an instantiation for: BOOM 1 must satisfy the following constraints: BOOM 1 must be a BOOM. Its MAX-SEA-STATE must be greater than or equal to 1 The possible instantiations for BOOM 1 are (BOOM1-OAKLAND-3000 BOOM2-RICHMOND-2000 BOOM3-CONCORD-1600 BOOM4-CONCORD-1250 BOOM5-MARTINEZ-1600 BOOM6-MARTINEZ-1000 BOOM7-MARTINEZ-1000 BOOM8-MARTINEZ-1000 BOOM9-MARTINEZ-1000 BOOM10-MARTINEZ-1000 BOOM11-OAKLAND-2400 BOOM12-CONCORD-400 BOOM13-MARTINEZ-300 BOOM14-MARTINEZ-600 BOOM15-MARTINEZ-2000 BOOM16-CONCORD-540 BOOM17-RICHMOND-200 BOOM18-OAKLAND-200 BOOM19-CARPINTERIA-1600 BOOM20-CARPINTERIA-10200 BOOM21-CARPINTERIA-1500 BOOM22-RICHMOND-1500 BOOM23-CARPINTERIA-3000).</p> </div> <div style="width: 50%;"> <div style="border: 1px solid black; padding: 5px; margin-bottom: 10px;"> <p><b>LOCATED</b> BOOM1-OAKLAND-3000 BERKELEY-EELGRASS [0,+00]--[0,+00]</p> </div> <div style="border: 1px solid black; padding: 5px; margin-bottom: 10px;"> <p><b>DEPLOY-BOOM</b> BOOM1-OAKLAND-3000 BERKELEY-EELGRASS 3000 [0,+00]--[0,+00]</p> </div> <div style="border: 1px solid black; padding: 5px; margin-bottom: 10px;"> <p><b>LOCATE-DEPLOY-BOOM3</b> BOOM2-RICHMOND-2000 BERKELEY-EELGRASS NORTH-ALAMEDA-COAST 2000 [0,+00]--[0,+00]</p> </div> <div style="border: 1px solid black; padding: 5px; margin-bottom: 10px;"> <p><b>LEVEL</b> BERKELEY-EELGRASS BOOM-LEVEL-1 8000 [0,+00]--[0,+00]</p> </div> <div style="border: 1px solid black; padding: 5px; margin-bottom: 10px;"> <p><b>BOOM-TEAM</b> 20 7 [0,+00]--[0,+00]</p> </div> <div style="border: 1px solid black; padding: 5px;"> <p><b>OVER-BY-GROUND</b> RICHMOND-PORT BERKELEY-EELGRASS 1 [0,+00]--[0,+00]</p> </div> </div> </div>																																																						
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>BOOM7-Martinez-1000 BOOM8-Martinez-1000 BOOM9-Martinez-1000 BOOM10-Martinez-1000 BOOM11-Oakland-2400 BOOM12-Concord-400 BOOM13-Martinez-300 BOOM14-Martinez-600 BOOM15-Martinez-2000</p> </div> <div style="width: 50%;"> <div style="border: 1px solid black; padding: 5px; margin-bottom: 10px;"> <p><b>BOOM3-CONCORD-1600 (any left click exits)</b></p> <table border="1" style="width:100%; border-collapse: collapse;"> <tr><td>Boom Make/Model</td><td>EXPANDI-BOOM-4300</td></tr> <tr><td>Location</td><td>I.T.VINEHILL-CONCORD</td></tr> <tr><td>Boom Length (Feet)</td><td>1600</td></tr> <tr><td>BOOM-DEPLOYMENT-HR</td><td>0.5</td></tr> <tr><td>Transportation</td><td>PWR-REEL-TRLR</td></tr> <tr><td>Boom Type</td><td>INFLATABLE</td></tr> <tr><td>Operating Environment</td><td>OCEAN</td></tr> <tr><td>Max. Sea State</td><td>4</td></tr> <tr><td>Boom Height</td><td>43</td></tr> <tr><td>Standard Length</td><td>50</td></tr> <tr><td>End Connectors</td><td>UNIVERSAL-SLIDE</td></tr> <tr><td>Boom Weight (lb/ft)</td><td>4</td></tr> </table> </div> <div style="border: 1px solid black; padding: 5px;"> <p><b>BOOM11-OAKLAND-2400 (any left click exits)</b></p> <table border="1" style="width:100%; border-collapse: collapse;"> <tr><td>Boom Make/Model</td><td>ABASCO-BETA-11A</td></tr> <tr><td>Location</td><td>O-NIEM-TOW-B40-OAKLAND</td></tr> <tr><td>Boom Length (Feet)</td><td>2400</td></tr> <tr><td>BOOM-DEPLOYMENT-HR</td><td>0.8</td></tr> <tr><td>Transportation</td><td>200-SECTS-STORAGE</td></tr> <tr><td>Boom Type</td><td>FOAM</td></tr> <tr><td>Operating Environment</td><td>INLAND</td></tr> <tr><td>Max. Sea State</td><td>2</td></tr> <tr><td>Boom Height</td><td>20</td></tr> <tr><td>Standard Length</td><td>200</td></tr> <tr><td>End Connectors</td><td>QUICK</td></tr> <tr><td>Boom Weight (lb/ft)</td><td>1.7</td></tr> </table> </div> </div> </div>							Boom Make/Model	EXPANDI-BOOM-4300	Location	I.T.VINEHILL-CONCORD	Boom Length (Feet)	1600	BOOM-DEPLOYMENT-HR	0.5	Transportation	PWR-REEL-TRLR	Boom Type	INFLATABLE	Operating Environment	OCEAN	Max. Sea State	4	Boom Height	43	Standard Length	50	End Connectors	UNIVERSAL-SLIDE	Boom Weight (lb/ft)	4	Boom Make/Model	ABASCO-BETA-11A	Location	O-NIEM-TOW-B40-OAKLAND	Boom Length (Feet)	2400	BOOM-DEPLOYMENT-HR	0.8	Transportation	200-SECTS-STORAGE	Boom Type	FOAM	Operating Environment	INLAND	Max. Sea State	2	Boom Height	20	Standard Length	200	End Connectors	QUICK	Boom Weight (lb/ft)	1.7
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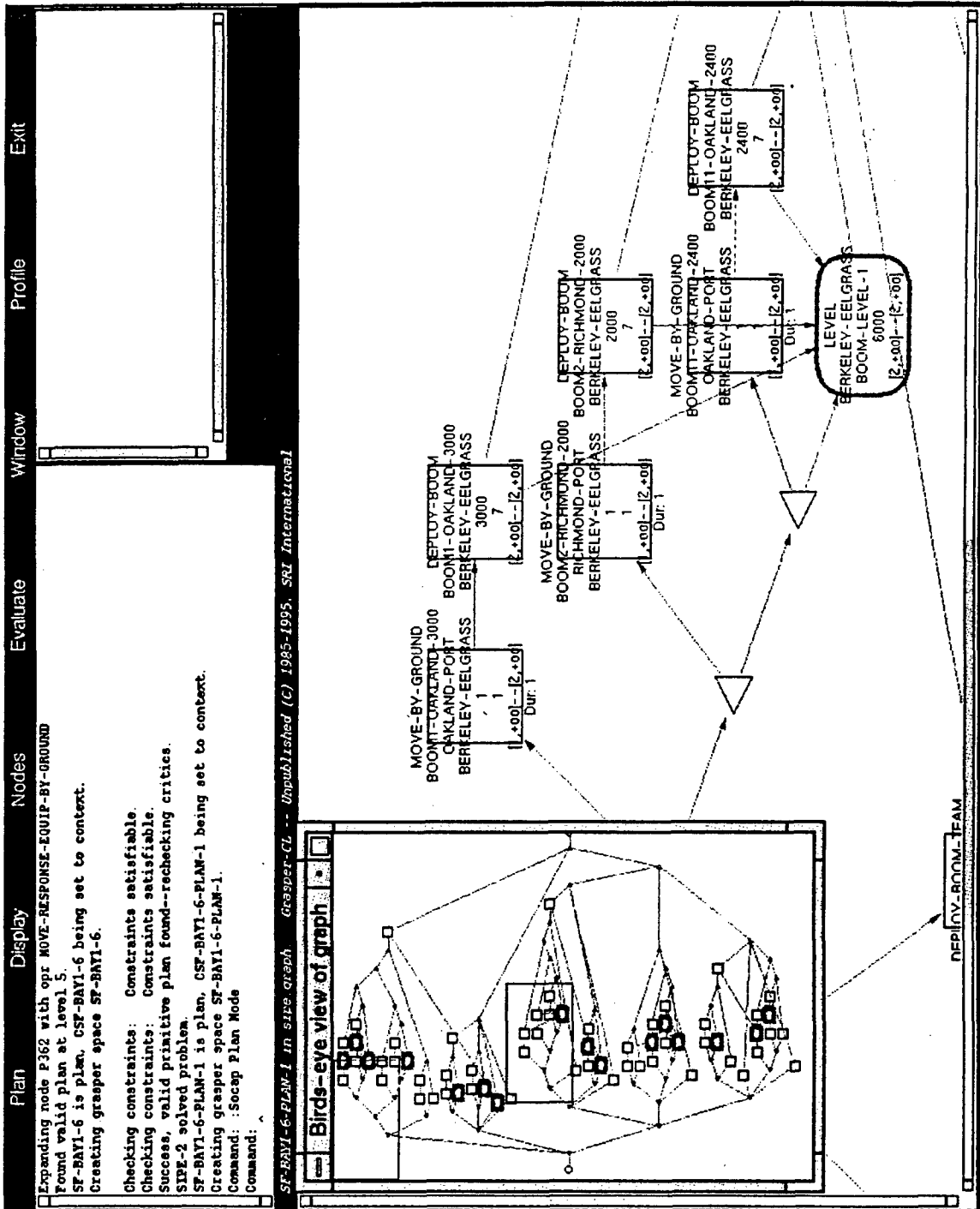


Resource Conflict Analysis					
Sort Units	Recompute	Redisplay	Analyze Capacity	Execute	Hardcopy
					Exit
VAC-TRUCK6-SF-1000	P363				
VAC-TRUCK6-SF-1000	P360				
VAC-TRUCK1-RICHMOND-1000	P388				
VAC-TRUCK2-RICHMOND-1000	Unused				
VAC-TRUCK3-SF-1000	P398				
VAC-TRUCK4-SF-1000	P355				
VAC-TRUCK5-SF-1000	P412				
VAC-TRUCK7-SF-1000	Unused				
VAC-TRUCK8-SF-1000	Unused				

**Days:**

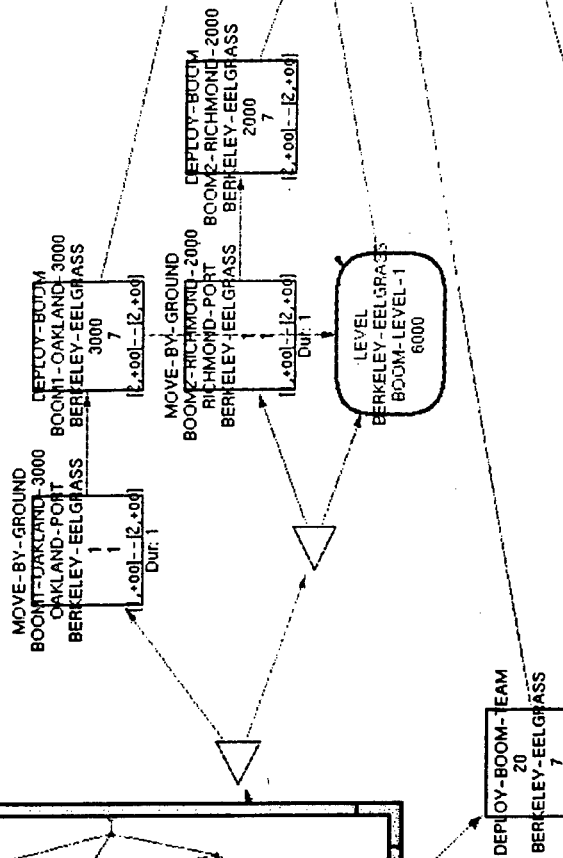
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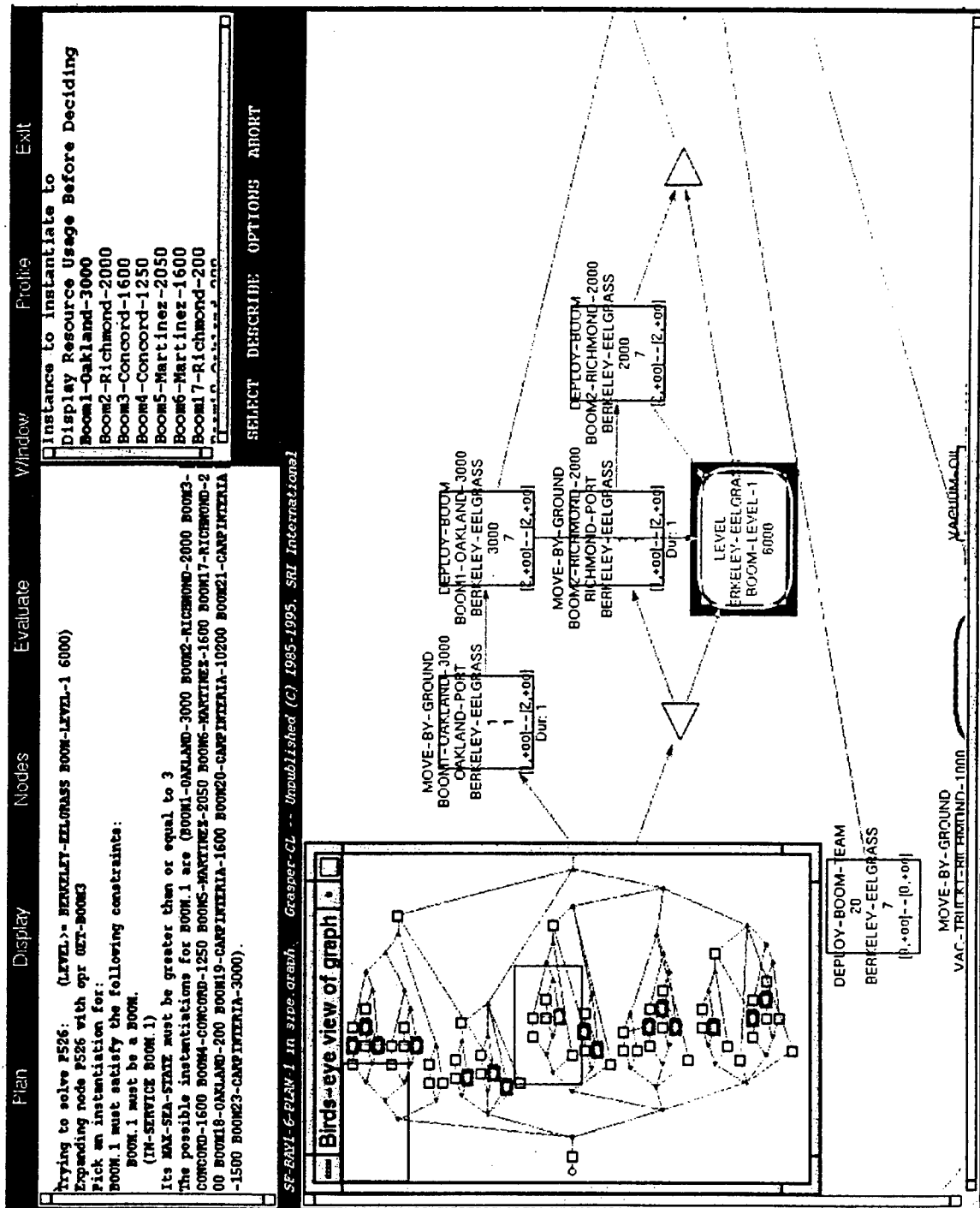
L: Click at this point; R: Menu.

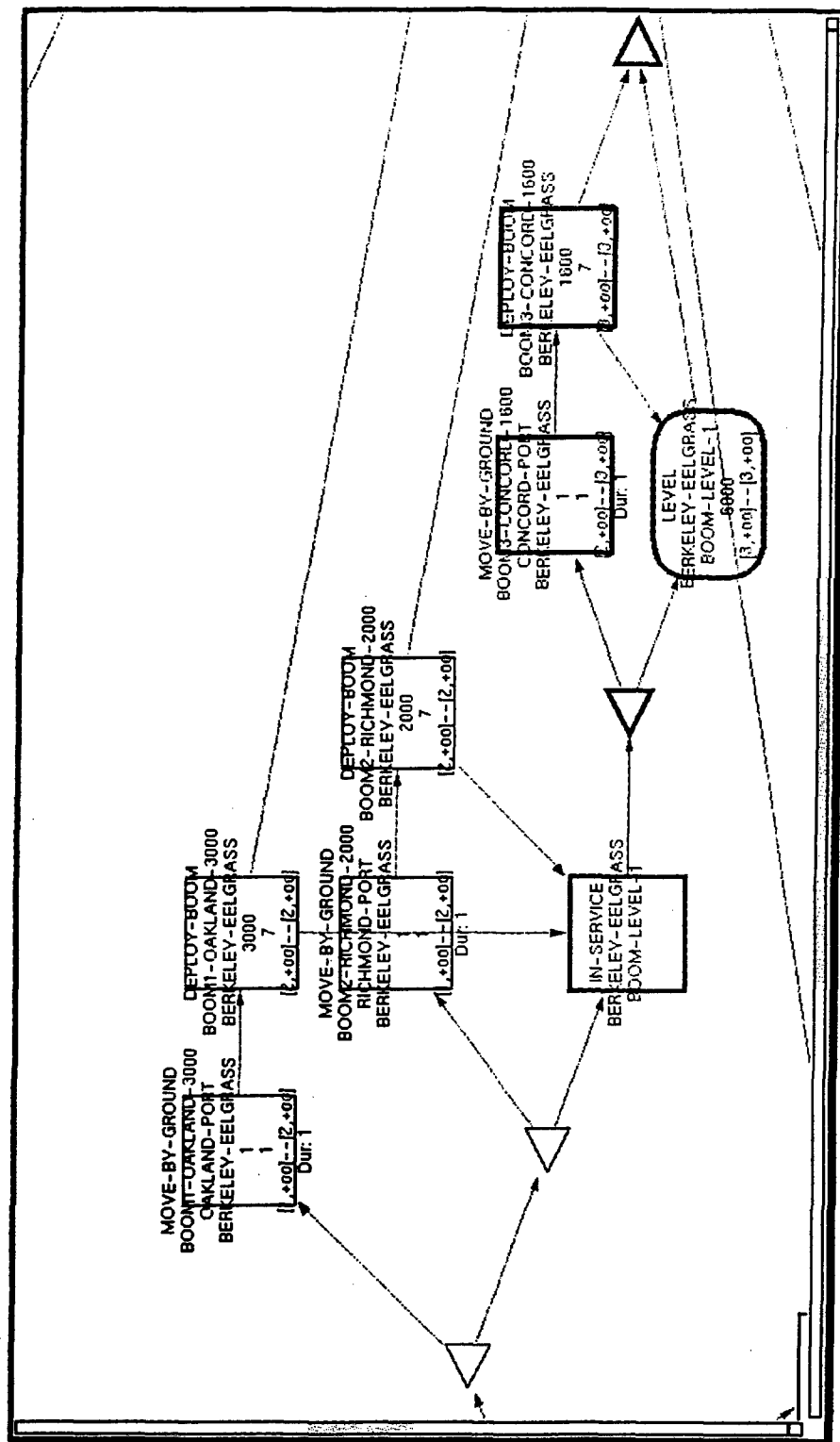


**Command:**

Grasper-CL -- Unpublished (c) 1985-1995, SRI International









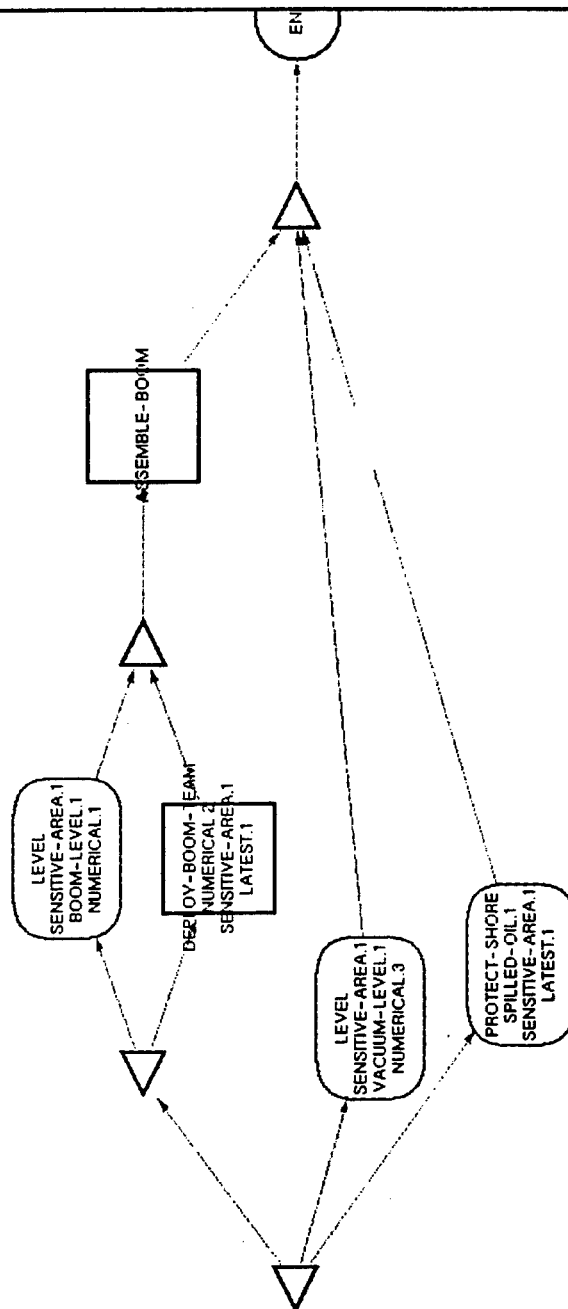
# SHORE-DIVERSION-BOOMING (any left click exits)

## PURPOSE:

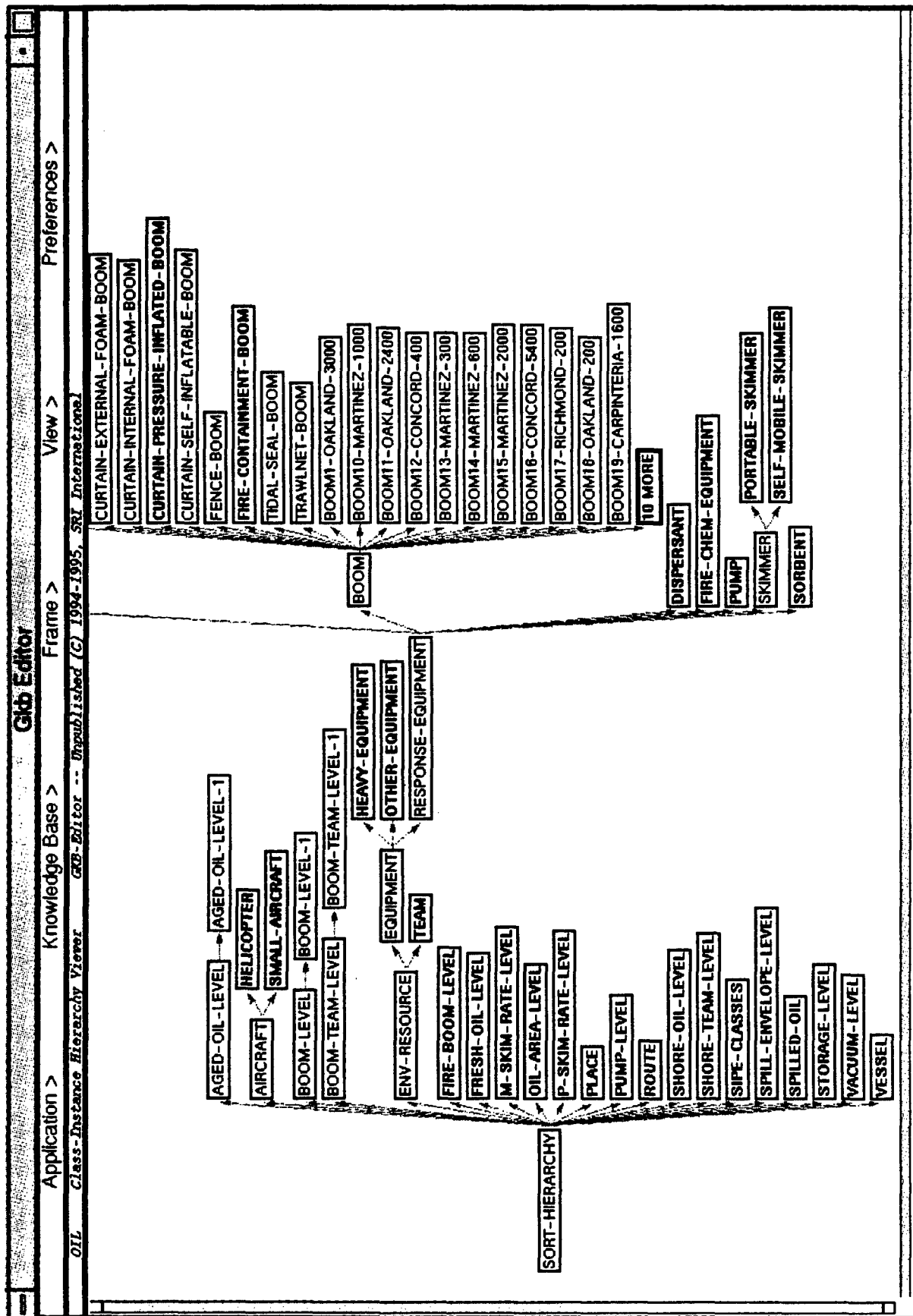
(PROTECT-SHORE SPILLED-OIL.1 SENSITIVE-AREA.1 LATEST.1)

## PRECONDITIONS:

SENSITIVE-AREA.1 is located within LAND-SECTOR.1  
(ADJACENT SEA-SECTOR.1 LAND-SECTOR.1)  
(AMOUNT-SPILLED-OIL.1 SEA-SECTOR.1 LATEST.1 NUMERICAL.3)  
(DIVERSION-BOOM-REQUIRED SENSITIVE-AREA.1 NUMERICAL.1)  
(BOOM-PERSONNEL-REQUIRED SENSITIVE-AREA.1 NUMERICAL.2)



Predicate Editor			
Copy Predicate	Delete Predicate	Edit Predicate	New Predicate Options Exit Pred Editor
<p>Command: :Exit Pred Editor</p> <p>Command: .</p>			
<p><b>COVERED SECTOR</b></p> <p>(COVERED-SECTOR SF-BAY-SPILL NORTH-ALAMEDA-COAST 3)</p> <p>(COVERED-SECTOR SF-BAY-SPILL SF-NORTH-COAST 1)</p> <p>(COVERED-SECTOR SF-BAY-SPILL GOLDEN-GATE 7)</p> <p>(COVERED-SECTOR SF-COAST-SPILL WEST-MARIN-COAST 12)</p> <p>(COVERED-SECTOR SF-COAST-SPILL GOLDEN-GATE 12)</p> <p>(COVERED-SECTOR SF-COAST-SPILL PACIFICA-COAST 24)</p> <p>(COVERED-SECTOR SF-COAST-SPILL MOSS-BEACH-COAST 36)</p> <p>(COVERED-SECTOR SF-COAST-SPILL PISCADERO-COAST 48)</p> <p>(COVERED-SECTOR SF-COAST-SPILL ANO-NUEVO-COAST 72)</p>			
<p><b>SEA STATE</b></p> <p>(SEA-STATE SF-NORTH-COAST 0 2)</p> <p>(SEA-STATE NORTH-ALAMEDA-COAST 0 1)</p> <p>(SEA-STATE EAST-MARIN-COAST 0 2)</p> <p>(SEA-STATE GOLDEN-GATE 0 3)</p> <p>(SEA-STATE SF-NORTH-COAST 1 2)</p> <p>(SEA-STATE NORTH-ALAMEDA-COAST 1 1)</p> <p>(SEA-STATE EAST-MARIN-COAST 1 2)</p> <p>(SEA-STATE GOLDEN-GATE 1 3)</p> <p>(SEA-STATE SF-NORTH-COAST 2 2)</p> <p>(SEA-STATE NORTH-ALAMEDA-COAST 2 1)</p> <p>(SEA-STATE EAST-MARIN-COAST 2 2)</p> <p>(SEA-STATE GOLDEN-GATE 2 3)</p> <p>(SEA-STATE SF-NORTH-COAST 3 2)</p>			
<p><b>EQUIPMENT LOCATIONS</b></p> <p>TUG-1 is located in NBO-SF-BAY-PORT.</p> <p>TUG-2 is located in MONTEREY-PORT.</p> <p>AIRCRAFT-1 is located in HALF-MOON-AIRFIELD.</p> <p>AIRCRAFT-2 is located in ALAMEDA-AIRFIELD.</p> <p>VAC-TRUCK1-RICHMOND-1000 is located in RICHMOND-PORT.</p> <p>VAC-TRUCK2-RICHMOND-1000 is located in RICHMOND-PORT.</p> <p>VAC-TRUCK3-SF-1000 is located in SAN-FRANCISCO.</p> <p>VAC-TRUCK4-SF-1000 is located in SAN-FRANCISCO.</p> <p>VAC-TRUCK5-SF-1000 is located in SAN-FRANCISCO.</p> <p>VAC-TRUCK6-SF-1000 is located in SAN-FRANCISCO.</p> <p>VAC-TRUCK7-SF-1000 is located in SAN-FRANCISCO.</p> <p>VAC-TRUCK8-SF-1000 is located in SAN-FRANCISCO.</p> <p>TRACTOR-1 is located in SAN-FRANCISCO.</p>			
<p><b>THREATENED SHORELINE</b></p> <p>(THREATENED-SHORELINE SF-BAY-SPILL BERKELEY-ELGRASS 7)</p> <p>(THREATENED-SHORELINE SF-BAY-SPILL RODEO-LAGOON 11)</p> <p>(THREATENED-SHORELINE SF-BAY-SPILL YERBA-BUENA-ISLAND 4)</p> <p>(THREATENED-SHORELINE SF-COAST-SPILL PISCADERO-BEACH 48)</p>			
<p><b>OK SEA STATE</b></p> <p>(OK-SEA-STATE SF-NORTH-COAST 0 2)</p> <p>(OK-SEA-STATE SF-NORTH-COAST 0 3)</p> <p>(OK-SEA-STATE SF-NORTH-COAST 0 4)</p> <p>(OK-SEA-STATE SF-NORTH-COAST 0 5)</p> <p>(OK-SEA-STATE SF-NORTH-COAST 0 6)</p> <p>(OK-SEA-STATE NORTH-ALAMEDA-COAST 0 1)</p> <p>(OK-SEA-STATE NORTH-ALAMEDA-COAST 0 2)</p> <p>(OK-SEA-STATE NORTH-ALAMEDA-COAST 0 3)</p> <p>(OK-SEA-STATE NORTH-ALAMEDA-COAST 0 4)</p> <p>(OK-SEA-STATE NORTH-ALAMEDA-COAST 0 5)</p> <p>(OK-SEA-STATE NORTH-ALAMEDA-COAST 0 6)</p> <p>(OK-SEA-STATE EAST-MARIN-COAST 0 2)</p> <p>(OK-SEA-STATE EAST-MARIN-COAST 0 3)</p>			
<p><b>AVAILABLE EQUIPMENT</b></p> <p>(AVAILABLE TUG-1 3)</p> <p>(AVAILABLE TUG-2 3)</p> <p>(AVAILABLE AIRCRAFT-1 1)</p> <p>(AVAILABLE AIRCRAFT-2 1)</p> <p>(AVAILABLE VAC-TRUCK1-RICHMOND-1000 1)</p> <p>(AVAILABLE VAC-TRUCK3-SF-1000 1)</p> <p>(AVAILABLE VAC-TRUCK4-SF-1000 1)</p> <p>(AVAILABLE VAC-TRUCK5-SF-1000 2)</p> <p>(AVAILABLE VAC-TRUCK6-SF-1000 2)</p> <p>(AVAILABLE VAC-TRUCK7-SF-1000 2)</p> <p>(AVAILABLE VAC-TRUCK8-SF-1000 2)</p> <p>(AVAILABLE TRACTOR-1 1)</p>			



**OIL SPILL PREVENTION THROUGH THE IMPROVED MANAGEMENT OF  
HUMAN ORGANIZATION ERRORS IN THE OPERATIONS OF TANKERS AND  
BARGES**

*Karlene H. Roberts, University of California*

### Background

For the last few years the Human and Organization Factors project at the University of California has been deeply immersed in a set of projects addressing various issues concerned with risk mitigation in the marine industry. A frequently heard comment in this industry is that eighty percent of the problems are caused by human error. Yet the vast majority of attention has gone to developing new and better "engineering tweaks" to problems. While members of the Berkeley team have focused on a number of engineering contributors to accident, their primary focus currently is on the human and organizational contributors to accidents. The team has worked with the U.S. Minerals Management Service, the California State Lands Commission, the U.S. Coast Guard, the American Bureau of Shipping, Chevron Shipping, ARCO Marine, Unocal, and the UKs Health and Safety Executive, to identify issues most crucial to preventing marine accidents. We have fleshed out many of the human and organizational contributors to accidents, identified problems with existing data bases and suggested changes that would make them more useful for identifying human and

organizational contributors to marine accidents. Examples of the kinds of reports, publications and presentations emerging from this project are:

#### Publications

Roberts, K.H. and M. Grabowski. (1996) "The Mutual Influence of Technological Advancement and other Organizational Processes." In S.R. Clegg, C. Hardy, and W. Nord (eds.) Handbook of Organization Studies. London: Sage, 409-423.

Bea, R.G. and K.H. Roberts. (1996) "Human and Organization Factors in Designs, Construction and Operation of Offshore Platforms." Journal of Petroleum Technology. Society of Petroleum Engineers. Richardson, TX.

#### Presentations

Bea, R. G., S. Stoutenberg, K.H. Roberts, T. Mannarelli, and P. Jacobson. "High Reliability Tanker Loading and Discharge Operations at the Chevron Wharf, Richmond, California." Ships Structure Committee (SSC), Society for Naval Architects and Marine Engineers (SNAME), Arlington, VA, November, 1996.

Bea, R.G. and K.H. Roberts. "Management of Rapidly Developing Crises: A Multi-Community Study." American Petroleum Institute Sixth Crisis Seminar, Crisis Management - Emergency Response and Risk Communication, Houston, TX, September, 1995.

Grabowski, M. and K.H. Roberts. "Risk Mitigation and Risk Mitigation in Waterways Systems." Annual Meeting of the Academy of Management, Vancouver, BC, August 1995.

Roberts, K.H. and R.G. Bea. "Organization Factors in Quality and Reliability of Marine Systems." Fourteenth International Conference on Offshore Mechanics and Arctic Engineering (OMAE 1995). Copenhagen, Denmark, June 1995.

Roberts, K.H. and R.G. Bea. "Organization Factors in Quality and Reliability of Marine Systems." Fourteenth International Conference on Offshore Mechanics and Arctic Engineering (OMAE 1995). Copenhagen, Denmark, June 1995.

Roberts, K.H. and R.G. Bea. "Organization Factors in Quality and Reliability of Marine Systems." Fourteenth International Conference on Offshore Mechanics and Arctic Engineering (OMAE 1995). Copenhagen, Denmark, June 1995.

Roberts, K.H. and R.G. Bea. "Organization Factors in Quality and Reliability of Marine Systems." Fourteenth International

Conference on Offshore Mechanics and Arctic Engineering (OMAE 1995). Copenhagen, Denmark, June 1995.

Moore, W.H., R.G. Bea, M. Grabowski, and K.H. Roberts. (June, 1995) "Managing Human and Organizational Error Through the Life Cycle of Offshore Marine Systems." Fourteenth International Conference on Offshore Mechanics and Arctic Engineering (OMAE 1995). Copenhagen, Denmark, June 1995.

Roberts, K.H. and R.G. Bea. "Organization Factors in Quality and Reliability of Marine Systems." Fourteenth International Conference on Offshore Mechanics and Arctic Engineering (OMAE 1995). Copenhagen, Denmark, June 1995.

Bea, R.G. and K.H. Roberts, "Evaluation of Human and Organization Factors in the Design, Construction, and Operations of Offshore Platforms." Offshore Technology Conference, Houston, TX, May, 1995.

Moore, W.H. and K.H. Roberts. "Safety Management for the Maritime Industry: The International Safety Management Code." 1995 International Oil Spill Conference: Achieving and Maintaining Preparedness. Long Beach, CA, February- March, 1995.

Roberts, K.H. "Up to Date: A Review of the University of California, Berkeley High Reliability Organizations and Human and Organizational Error Projects." University College, Dublin, Ireland, November, 1994.

### Reports

Boniface, D.E. (1995) "Assessing the Risks and Countermeasures for Human and Organizational Error in the Marine Industry," Master's Thesis, University of California at Berkeley, Naval Architecture.

Mason, E., K.H. Roberts, and R. Bea, (1995) "Reduction of Tanker Oil and Chemical Spills: Development of Accident and Near-Miss Data Bases. Report to the California Sea Grant College.

Moore, W. (1993) "Management of Human and Organizational Error in Operations of Marine Systems," Doctoral Dissertation, University of California at Berkeley, Naval Architecture.

Stoutenberg, S., and R. Bea, (1995) "Reduction of Tanker Oil and Chemical Spills: Engineering to Minimize Human and Organizational Errors." Report to the California Sea Grant College.

### Current Work

The original research proposal to Department of Transportation suggested that we continue to look at a variety of human and

organizational issues that impact risk in the marine industry. However, for some time other organizations have been claiming to us that they face the same or similar challenges in preventing risk faced by the marine industry. While we began our investigations many years ago focusing solely on organizations in which error could have catastrophic consequences, a number of other organizations are beginning to see themselves as having to behave in ways designed to produce nearly error free operations. Their appear to be at least three reasons for this: increased litigation and increased expense of litigation; the environmental movement; and the desire to avoid "CNN time" or better yet, "Sixty Minutes time."

After the DOT grant was made we requested that we change the focus of the research some to include other types of organizations from whom we felt the marine industry could learn more about risk mitigation, and particularly about reducing human error and designing organizations that would better accommodate safe human practices. Our request was accepted.

The one year research support from DOT allowed us to 1) identify a community of organizations which face operational challenges similar to those faced in the marine industry, 2) refine a model of risk mitigation to test across communities of organizations and to define a research area emanating from our recent work, and 3) bring people in those communities together to begin to gain "lessons learned" from each other.

#### **Identifying "Communities" to Participate**



We engaged in a number of conversations, beginning with people we know who were concerned about risk in their workplaces, and letting them identify for us other people with similar concerns (the sampling theorists call this "snowball sampling."). The organizations participating with us currently are:

**Commercial aviation:** The Federal Aviation Administration, United Airlines, Delta Airlines, Boeing Commercial Airplane Group.

**Military aviation:** the United States Navy and Marine corps aviation communities.

**The Marine Industry:** The U.S Coast Guard, U.S. Minerals Management Service, California State Lands Commission, American Bureau of Shipping, UNOCAL, Chevron, ARCO Marine, the Health and Safety Executive of the United Kingdom.

**Policing (particularly with reference to hostage and terrorist negotiation):** The Oakland Police Department, the East Bay Regional Park System (which is engaged in preliminary discussion with the FBI).

**Medical Emergency Situations:** The Loma Linda University Pediatric Cardiology unit (discussions are in process with UCLAs ICUs).

We expect contributions in one way or another from each organization. However, we do not expect each to contribute in kind. Some are a part of the research, some support the workshops which offer settings for exchange of "lessons learned."

#### **Current Research Issues**

Two general streams of research are underway. We hope this set will expand in years to come. The first has its etiology in a PhD. thesis done at the University of California at Los Angeles. The second is based on some findings from our most recent research that trouble us.

**The UCLA project.** For her PhD. thesis, Dr. Carolyn Libuser developed a risk management model, claiming that organizations

which did not attend the factors in her model were more subject to risk than were organizations that attend these factors. She initiated her work by studying five technologically advanced organizations that failed catastrophically (Exxon Valdez, Chernobyl, Union Carbide's plant at Bhopal, the Hubble telescope, and the Space Shuttle Challenger). Using primary reports of these accidents she teased out a set of factors she felt failed to operate in each setting.

Because she wanted to rule out the effects of advanced technology and see if her factors operated or failed to operate without the technological encumbrance, she solicited research participation from ten banks, five of which had failed and five of which were successful. Her model was supported. The failing banks failed to have in place the characteristics Dr. Libuser calls for if organizations are to mitigate risk, the successful banks had these factors in place. The factors are:

**1. Process Auditing:** An established system for ongoing checks designed to spot expected as well as unexpected safety problems. Safety drills are included in this category as is equipment testing. Followups on problems revealed in prior audits are a critical part of this section as well.

**2. Reward System:** The reward system is the payoff an individual or an organization obtains for behaving one way or another. In this case we are concerned with risky behavior. Organizational theory points out that an organization's reward system tends to have a powerful influence on the behavior of its individuals. Similarly, inter organizational reward systems also influence behavior in organizations.

**3. Degradation of Quality and/or Inferior Quality:** This refers to the essential quality of the system involved as compared to a referent system that is generally regarded as the standard for quality.

**4. Perception of Risk:** Two elements of risk perception are

involved here. (1) Whether or not there is any knowledge risk exists at all, and (2) If there is knowledge risk exists, the extent to which it is acknowledged appropriately and/or minimized.

**5. Command and Control:** This factor is borrowed from Roberts (1989, 1988, 1992). Roberts delineates command and control elements as separate factors, but we combine them here and list separate factors as sub factors in the broader model. The command and control elements are:

- a. Migrating decision making (the person with the most expertise makes the decision.
- b. Redundancy (people and/or hardware), i.e. backup systems exist.
- c. Senior managers who can see the "big picture", i.e. they don't micromanage.
- d. Formal rules and procedures. A definite existence of hierarchy but not necessarily bureaucracy in the negative sense.
- e. Training

Many managers we've shown the model think it workable in their industry. We are working to publish the model in an academic outlet. One publication speaks to issues in the model:

Roberts, K.H. and Libuser, C (1993) "From Bhopal to Banking: Organization Design Can Mitigate Risk," Organizational Dynamics, 21, 15-26.

The United States Navy is attempting to better operationalize the model and assess its aviation community's effectiveness using it.

**A systems perspective.** The other research agenda is directly derived from accumulating information from our own work that suggests that organizations in which errors can have very serious consequences in terms of loss of life, production, and the ecology, operate as systems. What happens in one part of the system effects what happens in other parts of the system, often to the dismay of managers. A system can be one organization. For example, policy made by the Coast Guard at headquarters surely influences its

operational units. But the system may be more accurately described as a group of organizations.

Two examples were strikingly presented to us by our participant organizations. It is fairly well known by now that Boeing Commercial Airplane Group worked with its customer, United Airlines, and other potential customers in designing the 777. In theory Boeing might have worked alone, but the product would not have been as satisfactory to any customer. Thus, a system was created. Similarly, an error was made at the Oakland Regional Traffic Center of the FAA which resulted in a small plane crashing in the East Bay Regional Park System. Suddenly two participants in our research were involved in a system.

The organizational literature fails entirely to discuss systems in this way. There is a body of macro sociological theory that "appears" to address issues of concern when one needs to think in these terms. That body of literature is remiss on a number of dimensions. Several of us are currently working to conceptualize how we might go about thinking about systems. Publications and presentations that touch on this issue are:

#### Publications

Grabowski, M. and K.H. Roberts (submitted for publication) "Risk Mitigation in Large Scale Systems: Lessons from High Reliability Organizations."

Mannarelli, Thomas, K.H. Roberts and R.G. Bea. (1996) "Learning How Organizations Mitigate Risk". Journal of Contingencies and Crisis Management.

Grabowski, M., and K.H. Roberts. (1996) "Human and Organizational Errors in Large Systems." IEEE Transactions on Systems, Man, and Cybernetics, 26, 2-16.

Weick, K.E., and K.H. Roberts. (1993) Collective mind and organizational reliability: The case of flight operations on an aircraft carrier deck. Administrative Science Quarterly, 38, 357-381.

### Presentations

Roberts, K.H. "Risk Mitigation in Communities of Organizations." Annual Meeting of the Academy of Management, Cincinnati, OH, August, 1996.

Roberts, K.H. "Ship Safety." Naval Research Advisory Committee Panel on Ship Maintenance and Damage Control, Arlington, VA, May, 1996

Roberts, K.H. "Best Practices in Crisis Management." Crisis, Planning, Management, and Communication Symposium, Strategic Research Institute, Denver CO, May, 1996.

Roberts, K.H. "Risk Mitigation in Systems of Organizations: Lessons from High Reliability Organizations." Crew Resource Management Best Practices Seminar, Boeing Commercial Airplane Group, Seattle, WA, January-February, 1996.

Roberts, K.H. "The Human Element: A Community Comparison." Foreign Vessel Industry Seminar, U.S. Coast Guard. Alameda, CA, January, 1996.

Roberts, K.H. (November, 1994) "Oil Spill Reduction: Organizations as Large Scale Systems." Washington State, Office of Marine Safety Annual Oil Spill Prevention Conference, November, 1994.

### **"Lessons Learned"**

The general idea driving the research is the same idea driving our activities in encouraging people from different industries to talk with each other, and encouraging researchers with different perspectives to engage one another (our team is interdisciplinary), the common thread being an interest in risk reduction. One activity in this arena is having senior researchers on the team discuss common challenges with participants in our group. Consistent with this we've met with Admiral James Card about his "prevention through people" program and with Captain

George Wright who is charged with carrying that program out.

We've also encouraged the development of a set of workshops that address a set of issues of common concern to their participants. These workshops have been supported by a variety of sources, including the Coast Guard. Our organizations sometimes tell us they are unable to support our research effort but can support a more modest effort in bringing people together. Here I list the workshops developed over the last year, and their sponsors. It would seem the Department of Transportation might have much to gain by joining some similar activities.

#### 1996 Workshops

Boeing Commercial Airline Group supported a two day workshop in January, 1996 that included participants from commercial aviation, marine, military, policing, fire, federal laboratories, petrochemicals, nuclear power, computer hardware, and medical care organizations. A major issue was the use of crew resource management (a strikingly successful strategy developed for aircraft crews by United Airlines) on aircraft design and manufacture.

The Marine Board of the National Academy of Science developed a set of three workshops that address various issues of marine safety. They're drawing on presentations from the nuclear power industry, Navy aviation, commercial aviation, training experts, human factors experts, incident reporting experts, etc. The last of this series of workshops is scheduled for early 1997. Financial support is provided by the U.S. Coast Guard, the American Bureau of Shipping and the U.S. Minerals Management Service.

Primatech is putting together a two day workshop in December, 1996, directed to marine industry participants. Presentations will be made by academicians and top level managers from other industries (including Ed Soliday, Vice President for Safety at UAL). Financial support is provided by the U.S. Minerals Management Service, the Health and Safety Executive (U.K.) American Bureau of Shipping, and major petroleum companies.